

# (19) United States

# (12) Patent Application Publication SIVANANTHAN et al.

# (10) Pub. No.: US 2010/0096001 A1

# (43) Pub. Date:

# Apr. 22, 2010

## (54) HIGH EFFICIENCY MULTIJUNCTION II-VI PHOTOVOLTAIC SOLAR CELLS

(75) Inventors: Sivalingam SIVANANTHAN, Naperville, IL (US); Wayne H.

LAU, Ann Arbor, MI (US); Christoph GREIN, Wheaton, IL (US); James W. GARLAND,

Aurora, IL (US)

Correspondence Address:

Momkus McCluskey, LLC 1001 Warrenville Road, Suite 500 Lisle, IL 60532 (US)

EPIR TECHNOLOGIES, INC., (73) Assignee:

Bolingbrook, IL (US)

Appl. No.: 12/261,827

(22) Filed: Oct. 30, 2008

## Related U.S. Application Data

Continuation-in-part of application No. 12/256,247, filed on Oct. 22, 2008, now abandoned.

#### **Publication Classification**

(51) Int. Cl. H01L 31/042

(2006.01)

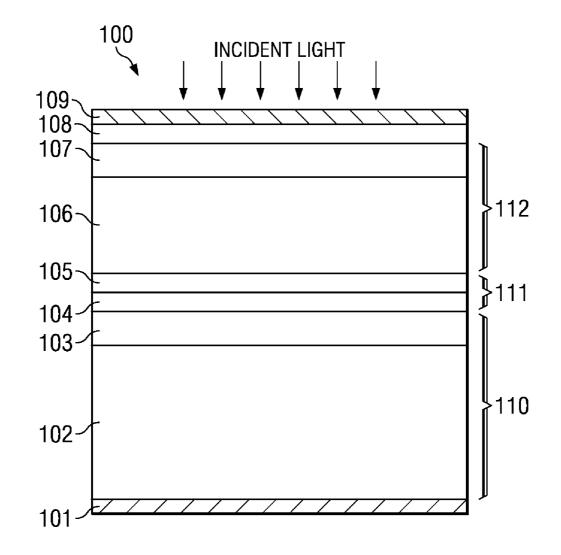
H01L 31/00

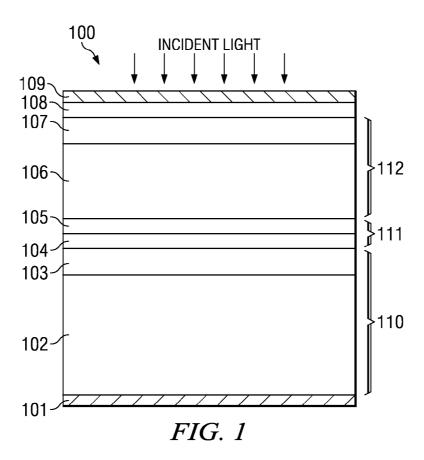
(2006.01)

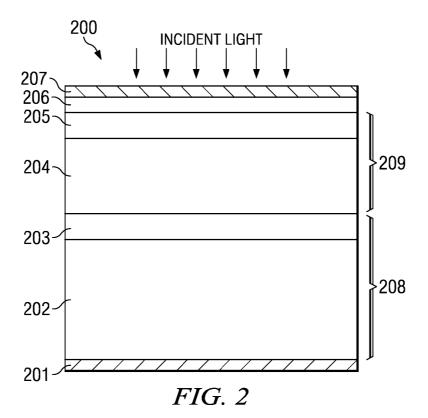
(52) **U.S. Cl.** ...... 136/249; 136/255; 136/261

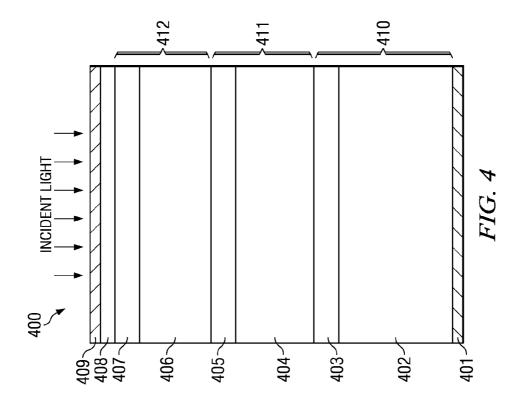
**ABSTRACT** 

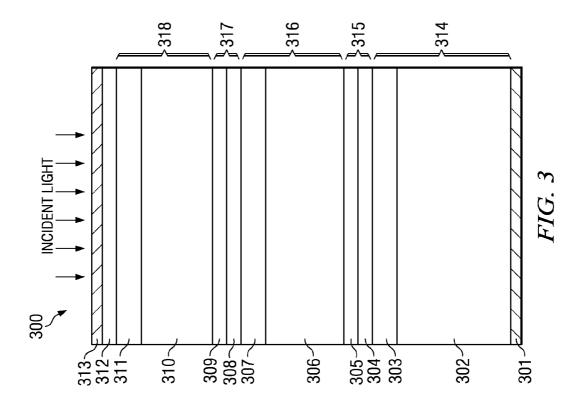
A Group II-VI photovoltaic solar cell comprising at least two and as many as five subcells stacked upon one another. Each subcell has an emitter layer and a base layer, with the base of the first subcell being made of silicon, germanium, or silicongermanium. The remaining subcells are stacked on top of the first subcell and are ordered such that the band gap gets progressively smaller with each successive subcell. Moreover, the thicknesses of each subcell are optimized so that the current from each subcell is substantially equal to the other subcells in the stack. Examples of suitable Group II-VI semiconductors include CdTe, ĈdSe, CdSeTe, CdZnTe, CdMgTe, and CdHgTe.

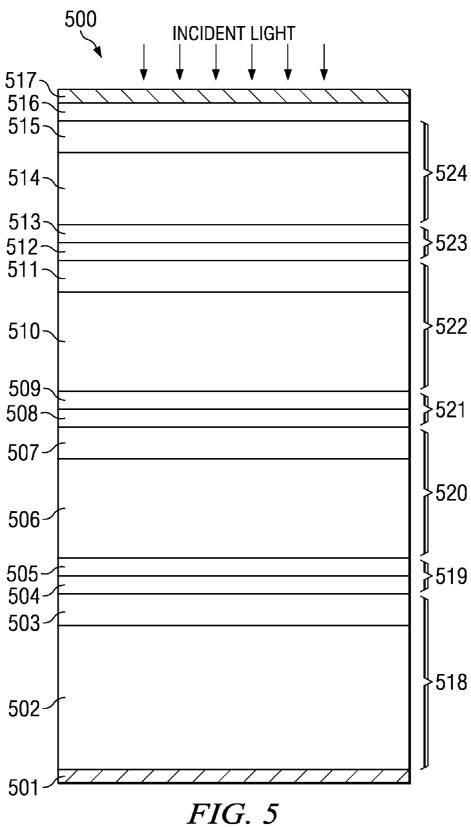


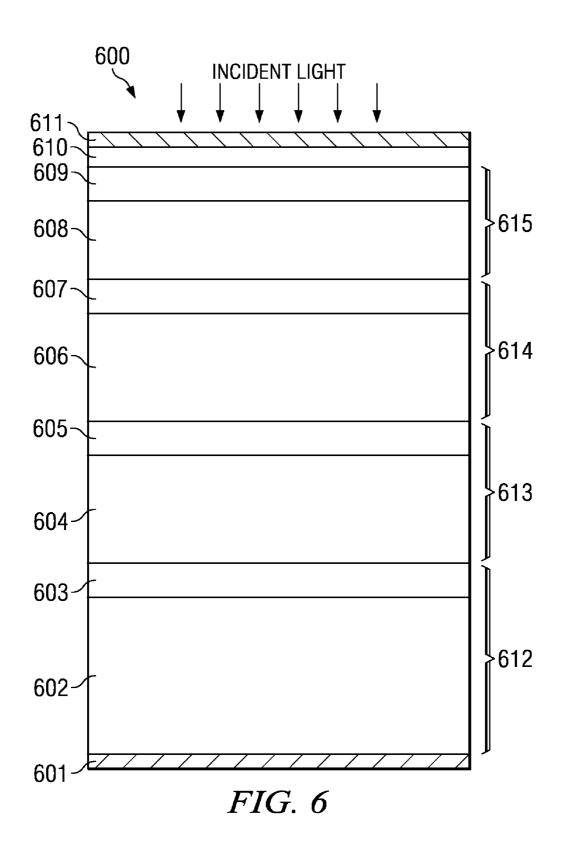


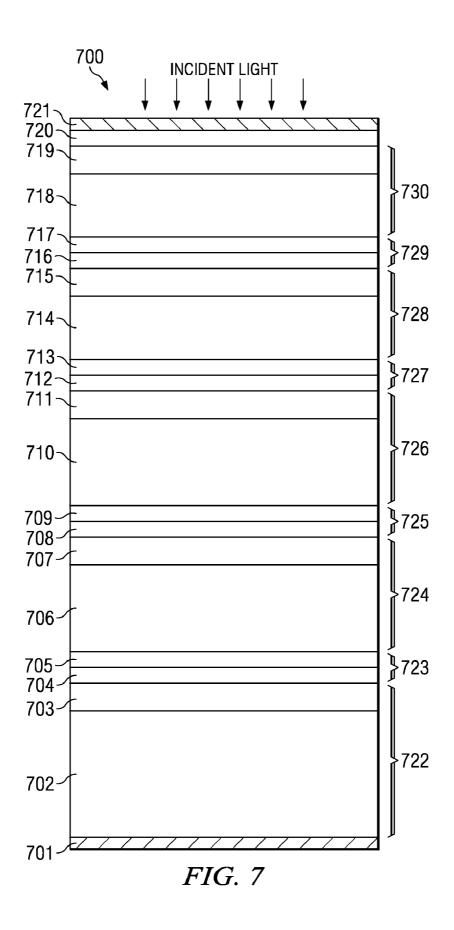


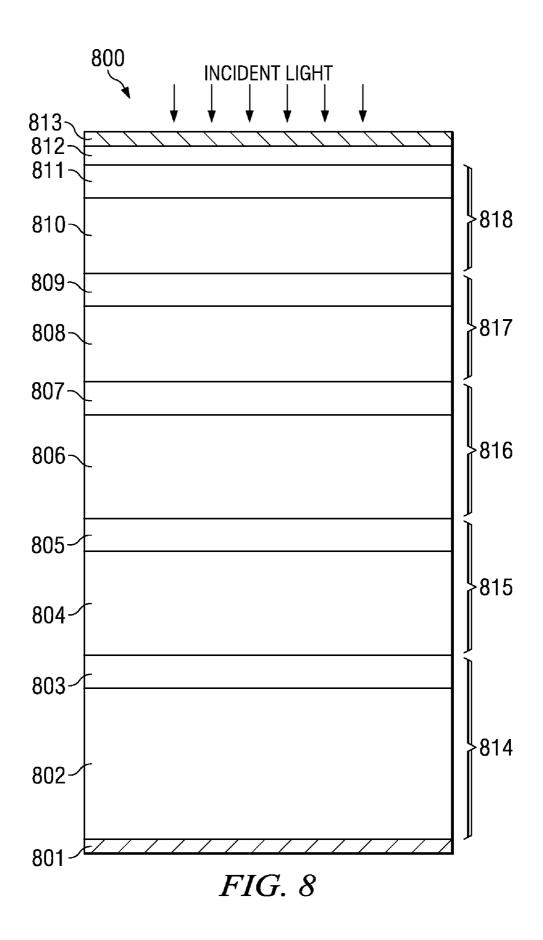












## HIGH EFFICIENCY MULTIJUNCTION II-VI PHOTOVOLTAIC SOLAR CELLS

## RELATED APPLICATIONS

[0001] This application is a continuation in part of U.S. patent application Ser. No. 12/256,247 filed 22 Oct. 2008, the specification of which is fully incorporated by reference herein.

## BACKGROUND OF THE INVENTION

[0002] Photovoltaic solar cells have many applications. Solar cell systems may be connected to an electric utility grid or be used independently. Applications include water heating, residential electric power, electric power for buildings, generation of power for electric utilities, applications in space, military applications, electric power for automobiles, airplanes, etc., and low-power specialty applications. Solar cells may be used in rooftop systems, in sheets rolled out on large flat areas in the desert or elsewhere, on systems that track the motion of the sun to gain the maximum incident solar power, with or without lenses and/or curved reflectors to concentrate the sun's light on small cells, in folding arrays on satellites and spacecraft, on the surfaces of automobiles, aircraft and other objects and even embedded in fabric for clothing, tents,

[0003] The primary function of a solar cell is to convert electromagnetic radiation, in particular solar radiation, into electrical energy. The energy delivered by solar radiation at the earth's surface primarily contains photons of energy hv in the range 0.7 eV up to 3.5 eV, mostly in the visible range, with hv related to the wavelength  $\lambda$  of the light by hv=1.24 eV/ $\lambda$  (µm). Although many photons of longer wavelength are incident at the earth's surface they carry little energy.

[0004] Most semiconductor devices, including semiconductor solar cells, are based on the p-n junction diode. In a semiconductor, the lowest conduction band and the highest valence band are separated by an energy gap,  $E_{\rm g}$ . A semiconductor is transparent to electromagnetic radiation with photons of energy hv less than  $E_{\rm g}$ . On the other hand, electromagnetic radiation with hv  $\geq E_{\rm g}$  is absorbed. When a photon is absorbed in a semiconductor, an electron is optically excited out of the valence band into the conduction band, leaving a hole (an absence of an electron in a state that normally is filled by an electron) behind. Optical absorption in semiconductors is characterized by the absorption coefficient. The optical process is known as electron-hole pair generation. Electronhole pairs in semiconductors tend to recombine by releasing thermal energy (phonons) or electromagnetic radiation (photons) with the conservation of energy and momentum.

[0005] When incident photons with energy equal to or greater than the energy gap of the semiconductor p-n junction diode are absorbed, electron-hole pairs are generated. Electron-hole pairs generated by the incident photons with energy greater than the band gap are called hot carriers. These photogenerated hot electrons and holes, which reside in the energy band away from the energy band zone center, rapidly give away their excess energy (the energy difference between the total carrier energy and the energy gap) to the semiconductor crystal lattice causing crystal lattice vibrations (phonons), which produce an amount of heat equal to the excess energy of the carriers in the semiconductor. As a result of the photogenerated electrons and holes moving in opposite directions under an electric field within the semiconductor p-n junction

diode, electron and hole photocurrents are simultaneously generated. Semiconductor devices based on this operating principle are known as photodiodes. Semiconductor photovoltaic solar cells are based on the same operating principle as the semiconductor p-n junction photodiodes described above. [0006] A conventional single p-n junction photovoltaic solar cell is composed of a very thick (p) and a very thin (n) semiconductor or vice versa. The thick (p-) doped absorber layer on the bottom of the photovoltaic solar cell is called the base, while the thin (n) layer on the top of the photovoltaic solar cell is called the emitter. The ideal efficiency of a photovoltaic solar cell is the percentage of power converted from the absorbed electromagnetic radiation to electrical energy. The photovoltaic solar cell energy conversion efficiency is partially determined by the band gap of the base layer semiconductor.

[0007] The advantage of a photovoltaic solar cell with a small energy gap base layer is that more incident photons are absorbed, and hence more electron-hole pairs are generated, producing a relatively high current in the solar cell. One disadvantage of such a photovoltaic solar cell is that the photovoltage is relatively low due to the small energy gap of the absorber. Another disadvantage of a small energy gap photovoltaic solar cell is that hot carriers are generated by the incident photons with energy much greater than the energy gap, and hence the excess energy of the hot carriers produces a large amount of heat in the thermalization process unless the higher energy photons are absorbed before reaching the narrow-gap material.

[0008] On the other hand, the advantage of a photovoltaic solar cell with a large energy gap base layer is that the output voltage of the photovoltaic solar cell is relatively high due to the large energy gap of the absorber. In addition, fewer hot carriers are generated because there are fewer photons with energy much greater than the energy gap. The disadvantage of such a photovoltaic solar cell is that a large number of incident photons have energies below the energy gap of the base layer semiconductor and hence are not absorbed, so that the output current is relatively low.

[0009] To achieve high energy conversion efficiency for a semiconductor photovoltaic solar cell, a high output voltage and a high current are required. In order to take advantage of narrow and wide band gap photovoltaic materials, a multifunction photovoltaic solar cell architecture approach is employed by stacking a number of photovoltaic solar cells with various base layer energy gaps. By connecting the photovoltaic solar cells in a serial fashion with the base layer energy gaps spanning the entire solar spectrum, optimal energy conversion efficiency could be achieved. But, in practice, the base layer energy gaps of a multijunction solar cell only cover a portion of the entire solar spectrum. To obtain maximum energy conversion efficiency in a multijunction photovoltaic solar cell, each individual solar cell (p-n junction diode) must be fabricated with high electrical and optical quality semiconductors, which can be achieved for lattice matched single-crystal semiconductor systems grown by molecular beam epitaxy (MBE), metal organic chemical vapor deposition (MOCVD), liquid phase epitaxy (LPE), or other epitaxial growth techniques.

[0010] In addition, the photocurrent generated in each individual solar cell is optimally identical to that in the others in order to maximize the energy conversion efficiency since the individual solar cells are connected in series and the photocurrent flows through each individual solar cell in a serial

fashion. Any excess current due to current mismatching among the individual solar cells is converted into heat in the multijunction photovoltaic solar cell. The photocurrent of a single p-n junction photovoltaic solar cell is proportional to the number of photons absorbed, which varies directly with the thickness and absorption coefficient of the base and emitter layers. Hence, the thicknesses of the semiconductor layers in a semiconductor multijunction photovoltaic solar cell must be properly designed based on the factors mentioned above in order to match the photocurrent generated in each individual solar cell.

[0011] Degenerately alloyed thin  $(p^{++})$  and  $(n^{++})$  tunnel junctions (TJ) are used as electrical circuit interconnects in a large number of multijunction photovoltaic solar cells to increase the solar energy conversion efficiency. The tunnel junctions are designed with minimal resistance and voltage drops across the junctions because the photovoltaic voltage of a multijunction solar cell is the sum of the photovoltaic voltage of the individual cells minus the voltage drops across the electrical circuit interconnects and contacts. A typical tunnel junction consists of an interface of heavily alloyed (p<sup>++</sup>) and (n<sup>++</sup>) layers with a narrow depletion layer in which a thin barrier is formed for electron tunneling. The separation of photo-generated electron-hole pairs due to the space-charge electric field induces a voltage drop across the tunnel diodes. In order to maximize the solar energy conversion efficiency, the voltage losses in the tunnel diodes must be minimized, and in addition the current of the individual photovoltaic cells must be matched. Under forward bias, electrons tunnel from the (n++) alloyed to (p++) alloyed layers, while electrons tunnel from (p++) alloyed to (n++) alloyed layers under reverse

[0012] To further improve the solar energy conversion efficiency of the photovoltaic solar cells, three-junction device structures have been employed. To date, Group III-V threejunction photovoltaic solar cells have been the most successful solar cell device architectures in terms of solar energy conversion efficiencies. Examples of such Group III-V threejunction photovoltaic solar cells are InGaP/GaAs/Ge and InGaP/InGaAs/Ge photovoltaic solar cells that are grown on Ge substrates by MBE or MOCVD. These cells have a conversion efficiency of approximately 40%. Other photovoltaic solar cell device structures with similar solar energy conversion efficiencies are the InGaP/GaAs/InGaAs three-junction photovoltaic solar cells grown on GaAs substrates by MBE or MOCVD. To optimize the total output current, degenerately alloyed (p++)GaAs/(n++) GaAs, (p++) AlGaAs/(n++) InGaP, and  $(p^{++})$ AlGaAs/ $(n^{++})$ GaAs tunnel junctions are often used. [0013] Multijunction photovoltaic solar cells with four, five, and six junctions grown on Ge substrates have been proposed to achieve solar energy conversion efficiency greater than 45%. Examples of such Group III-V cells include AlInGaP/AlInGaAs/InGaAs/Ge, AlInGaP/AlInGaAs/In-GaAs/InGaNAs/Ge, and AlInGaP/InGaP/AlInGaAs/In-GaAs/InGaNAs/Ge. The tunnel junctions used in these multijunction photovoltaic solar cells are similar to those used in the three-junction photovoltaic solar cells described above.

[0014] Important considerations for achieving high-efficiency energy conversion include the following: a) high quality crystalline layers; b) an appropriate choice of junction band gaps based on the impinging solar spectrum; c) tunnel junction interconnects between p-n junctions; d) an appropriate choice of layer thicknesses to achieve a current-matched

structure; and e) passivating layers, such as back-surface-field layers or window layers, to reduce losses.

[0015] In the past, high-efficiency III-V semiconductor multi-junction solar cells have been grown on GaAs, InP, and Ge substrates, but silicon substrates are advantageous for reasons of cost and mechanical robustness. The current multijunction single-crystal III-V solar cells grown on Ge substrates cost approximately \$13/cm², compared with approximately 2¢/cm² for crystalline Si solar cells. However, sunlight incident on a small solar cell can be multiplied by a factor of 600 in a concentrator photovoltaic (CPV) system that tracks the sun to an accuracy of better than 1°. Thus, the cell cost per watt of electric power produced by a multijunction cell in a CPV system can be less than that of a Si cell in a flat plate system.

[0016] Previous efforts on the development of multijunction single-crystal solar cells have focused almost entirely on III-V materials for two compelling reasons. First, according to the commonly accepted wisdom, epitaxial growth is best performed on lattice matched substrates and on lattice matched epilayers, and it is very difficult to lattice match substrate material for the growth of appropriate II-VI layers for solar cells, whereas the GaInP/GaAs/Ge system is almost perfectly lattice matched and has an almost ideal set of energy gaps for a three-junction solar cell. See U.S. Pat. Nos. 6,657, 194 and 6,906,358, which are specifically incorporated by reference.

[0017] Second, III-V materials and their doping and contacting are very familiar to many workers because of their widespread use in the electronics industry, whereas II-VI materials have been used only on a much more limited basis. Some representative patents for III-V based solar cells for CPV systems and previous cells using GaAs substrates are U.S. Pat. Nos. 4,163,987, 4,191,593, 4,206,002, 4,332,974, 4,575,577, 4,667,059, 4,926,230, 5,009,719, 5,342,453, 5,405,453, 5,853,497, 6,147,296, 6,252,287, 6,281,426, 6,300,557, 6,300,558, 6,660,928, 6,951,819, and 7,217,882. [0018] In general, even a completely successful growth of a three-junction single-crystal III-V solar cell on Si would not

three-junction single-crystal III-V solar cell on Si would not solve all of the problems associated with multifunction III-V solar cells. In particular, the growth of III-V materials by MOCVD using hydrogen, arsine, phosgene and the other necessary precursor gases introduces a number of difficulties. This method of growth requires elaborate safety precautions and makes regulatory approval difficult. Also, in this method deposits appear rapidly in the growth chamber, which combined with the nature of the deposits implies high maintenance costs and much down time. These considerations make the development of II-VI multifunction single-crystal cells grown by MBE, as proposed in the present invention, very desirable.

[0019] The number of relevant patents dealing with Group II-VI solar cells is very limited. U.S. Pat. No. 4,710,589 teaches a heterojunction p-i-n photovoltaic cell having at least three different semiconductor layers formed of at least four different elements comprising a (p-) relatively wide band gap semiconductor layer, a high resistivity intrinsic semiconductor layer, used as an absorber of light radiation, and an (n) relatively wide band gap semiconductor layer. In the preferred embodiment ZnTe is employed as the (p) layer, CdTe as the intrinsic absorber layer, and CdS as the (n) layer.

[0020] U.S. Pat. No. 4,753,684 proposes a cell having only a single polycrystalline absorber layer. The proposed cell structure includes a relatively wide optical bandgap energy

window layer, a light-absorbing layer and a third, relatively wide bandgap energy layer that forms a minority carrier mirror with the light-absorbing layer. It is realized using II-VI semiconductor compounds such as a CdS or ZnS window layer, a HgCdTe, CdTe, ZnCdTe or HgZnTe light absorbing layer and a third layer of CdTe, ZnTe, ZnCdTe, HgZnTe or CdMnTe. Cd and Te are present in at least two of the three layers of the proposed structures.

**[0021]** U.S. Pat. No. 6,419,742 proposes a method for the growth of high quality lattice mismatched II-VI semiconductor epitaxial layers on Si. This third patent proposes the formation of a passivation layer on a Si surface before the MBE growth of a II-VI material such as CdS. The passivation layer may comprise arsenic, germanium or  $\text{CaF}_2$ .

[0022] Thus, there exists a need for low cost, highly efficient solar cells to help meet the power needs of the future. If ultrahigh efficiency multifunction II-VI solar cells could be manufactured by MBE using Si substrates, their manufacture would be easier to scale up than the manufacture of the corresponding III-V cells and would be substantially less expensive than even the corresponding III-V cells grown on Si substrates.

[0023] The only public disclosure of significant relevance to this invention originated from the first inventor, Prof. S. Sivananthan. He contracted Prof. M. Flatte of the University of Iowa to perform calculations of the possible theoretical efficiency of II-VI HgCdZnTe solar cells. The idea was confined to single-junction and two-junction solar cells with an unspecified substrate which was not an active part of the solar cell. There was no thought of applications to CPV systems or to applications in space. No publications resulted, only a workshop talk on the calculations by one of Prof. Flatte's students: "HgCdZnTe Materials for High-Efficiency Tandem Solar Cells", B. Brown, M. E. Flatté, P. Boieriu, and S. Sivananthan, the 1998 U.S. Workshop on the Physics and Chemistry of II-VI Materials, Charleston, S.C., Oct. 21, 1998. No printed publication of these calculations was made and there was insufficient information in the art at the time to reduce these cells to practice.

# SUMMARY OF THE INVENTION

[0024] The present invention generally relates to a Group II-VI photovoltaic solar cell having at least two and as many as five subcells that gives conversion efficiencies approximately as good as or better than the best previously achieved using other semiconductor families. The subcells use combinations of materials that are easier and much less expensive to manufacture. These solar cells can be manufactured by MBE at a cost less than one fifth that of existing or previously proposed multifunction solar cells having similar efficiencies

[0025] In one aspect of the present invention, a monolithic multifunction photovoltaic solar cell comprises a first and a second subcell. The first subcell has a first base and a first emitter formed of opposite conductivity types, and the second subcell has a second base and a second emitter formed of opposite conductivity types. At least one of the bases and emitters is formed of a Group IV semiconductor material. At least one of the bases and emitters is formed of a Group II-VI semiconductor material. When incident solar radiation of a predetermined intensity not absorbed in the second (top) subcell impinges on the upper face of the first subcell, the current density of the photovoltaic current generated in the first sub-

cell will be substantially the same as the current density from this radiation generated in the second subcell.

[0026] In further embodiments of the invention, third, fourth and fifth subcells can be formed with respective third, fourth and fifth bases and emitters, the alloying and thickness of all of the bases and emitters being controlled such that the current density in any one of the subcells substantially matches the current density of the rest. It is preferred that the base of the first subcell be formed from a silicon substrate while the rest of the solar cell be grown from II-VI semiconductor materials, such as CdS, CdSe, CdTe, ZnTe, ZnS, MgTe, CdSeTe, CdZnTe, CdMnTe, CdMgTe and CdHgTe. It is also preferred that an antireflection layer be formed above the topmost subcell from a material selected from the group consisting of Cd<sub>2</sub>SnO<sub>4</sub>, SnO<sub>2</sub>, ZnSe, TiO<sub>2</sub>, MgTe, ZnO, ZnS, MgSe, ITO, MgS, MgO, SiO<sub>2</sub> and MgF<sub>2</sub>.

[0027] In a further aspect of the invention, a monolithic multijunction photovoltaic solar cell is provided which has at least first and second subcells, each with respective bases and emitters formed to be of opposed conductivity types. At least one of the first and second bases and the first and second emitters is formed of a Group IV semiconductor material, while at least one of the first and second bases and the first and second emitters is formed of a Group II-VI semiconductor material. None of the bases or emitters are formed of Group III-V semiconductor material. The solar cell has an ideal series energy conversion efficiency of at least approximately 40%.

[0028] It is preferred that this solar cell further include a first tunnel junction between the first and second subcells, with an energy gap of at least one of its layers being greater than the energy gap of the first base.

[0029] This provided solar cell can likewise include third, fourth and even fifth subcells. Preferably, tunnel junctions are formed between adjacent subcells. With three subcells, in theory an overall ideal series efficiency of 40% can be achieved under concentrated sunlight, such as 500 suns. This is approximately the same as the theoretical efficiency of a Group III-V solar cell with three subcells, calculated under the same assumptions. According to the invention, this number rises to 45% for structures with four subcells under 500 suns, and 50% for cells with five subcells under 500 suns. Indeed, the invention provides numerous photovoltaic solar cell embodiments having no Group III-V semiconductors but still having overall ideal series efficiencies in excess of 45% in theory under 500 suns illumination.

[0030] In another embodiment of the invention, a monolithic multijunction photovoltaic solar cell comprises a first subcell comprising a first base formed of a semiconductor having a first base energy gap and an emitter formed to adjoin the first base and having a first emitter energy gap higher than the first base energy gap. The solar cell includes at least a second subcell formed over the first subcell and comprising a second base formed of a Group II-VI semiconductor material and having a second base energy gap higher than that of the first base, and a second emitter formed of Group II-VI semiconductor material formed to adjoin the second base and having a second emitter energy gap higher than of the first emitter.

[0031] In a still further aspect of the invention, a monolithic multijunction photovoltaic solar cell is provided which has at least first and second subcells, with the second subcell being formed over the first. The first subcell includes a first base of a first conductivity type and a first emitter of an opposite

conductivity type. The second subcell likewise includes a second base of the first conductivity type and a second emitter of the opposite conductivity type. The second base and emitter are formed of Group II-VI semiconductor material. The energy gap of the second base is higher than the energy gap of the first base, while the energy gap of the second emitter is higher than the energy gap of the first emitter. It is preferred that the first base of this cell be formed of a Group IV semiconductor material, such as Si, Ge or mixtures thereof.

[0032] This solar cell can also be built with third, fourth and even fifth subcells over the first and second subcells. Bandgaps of the bases of such subcells will be higher than bandgaps of the bases below them. Similarly, energy bandgaps of the emitters of such subcells will be higher than the bandgaps of the emitters formed below them. The additional subcells are formed of Group II-VI semiconductor materials, preferably by an MBE method.

[0033] As in the other embodiments, it is preferred that degeneratively alloyed tunnel junctions be formed between adjacent ones of the subcells, and that the subcell stack be capped with an antireflective coating with a bandgap higher than that of the subcell layer beneath it. This antireflective coating prevents damage from overly energetic impinging photons and is particularly important in outer space or other high-radiation environments.

#### BRIEF DESCRIPTION OF THE DRAWINGS

[0034] Further aspects of the invention and their advantages can be discerned in the following detailed description, in which:

[0035] FIG. 1 is a highly magnified schematic elevational sectional view of a two junction photovoltaic solar cell according to a first embodiment of the present invention;

[0036] FIG. 2 is a highly magnified schematic elevational sectional view of a two junction photovoltaic solar cell according to a second embodiment of the present invention, without tunnel junctions disposed between the subcells;

[0037] FIG. 3 is a highly magnified schematic elevational sectional view of a three junction photovoltaic solar cell according to a third embodiment of the present invention;

[0038] FIG. 4 is a highly magnified schematic elevational sectional view of a three junction photovoltaic solar cell according to a fourth embodiment of the present invention without tunnel junctions disposed between the subcells;

[0039] FIG. 5 is a highly magnified schematic elevational sectional view of a four junction photovoltaic solar cell according to a fifth embodiment of the present invention;

[0040] FIG. 6 is a highly magnified schematic elevational sectional view of a four junction photovoltaic solar cell according to a sixth embodiment of the present invention without tunnel junctions disposed between the subcells;

[0041] FIG. 7 is a highly magnified schematic elevational sectional view of a five junction photovoltaic solar cell according to a seventh embodiment of the present invention; and

[0042] FIG. 8 is a highly magnified schematic elevational sectional view of a five junction photovoltaic solar cell according to a eighth embodiment of the present invention without tunnel junctions disposed between the subcells.

# DETAILED DESCRIPTION

[0043] The multijunction photovoltaic solar cell of the invention may comprise a plurality of subcells each of which

convert solar radiation into electrical energy. In various preferred embodiments of the multijunction photovoltaic solar cell, the subcells with different energy gaps absorb different components of the solar radiation spectrum enabling more efficient conversion of incident solar energy into electrical energy. The subcells comprise material systems of different energy gaps corresponding to different optical absorption cutoff energies such that incident light in different spectral ranges is efficiently absorbed by the different subcells. The subcells with larger energy gaps are stacked on top of the subcells with smaller energy gaps so that the upper subcells absorb the photons of the incident light with energies equal to or greater than the energy gaps of the upper subcells allowing the unabsorbed photons of the incident light to be transmitted through the upper subcells and subsequently absorbed by the lower subcells with smaller energy gaps. In preferred embodiments of the present invention, relatively high energy gap tunnel junctions that are used as low-resistance electrical circuit interconnects are placed between the subcells. Solar cells according to the present invention provide higher opencircuit photovoltages and higher short-circuit photocurrent densities as well as lower series resistance losses. The solar cells of the present invention also facilitate current matching through each of the subcells to increase solar energy conversion efficiency.

[0044] Without limitation, the present invention is applicable to photovoltaic solar cells for both terrestrial and non-terrestrial applications, photodiode detectors, light-emitting diodes, and semiconductor diode lasers.

[0045] Various embodiments of the present invention involve fabricating a monolithic photovoltaic solar cell comprising a plurality of the subcells in a fabrication sequence wherein the lower subcells with small energy gaps are usually fabricated first, while the upper subcells with larger energy gaps are subsequently fabricated on the top of the lower subcells. The subcells of the present invention can be fabricated by material growth methods such as MBE, MOCVD, and LPE. Layer thicknesses and alloying of the semiconductor thin layers that form the subcells of the multijunction photovoltaic solar cell can be controlled and optimized by adjusting the different raw material compositions, flux rates and deposition durations during the growth to meet the requirements of the specific design for a photovoltaic solar cell.

[0046] In the exemplary cell 100 illustrated in FIG. 1, a first subcell 110, which is made of a first material system, comprises a first (p)Si base layer 102 and a first (n)Si emitter layer 103 having a first base energy gap ( $E_{g1B} \approx 1.10 \text{ eV}$ ), a first emitter energy gap ( $E_{g1E} \approx 1.10 \,\text{eV}$ ), and a first layer thickness  $(d_1 \approx 1.0 \text{ to } 500 \,\mu\text{m}, \text{ preferably greater than } 2 \,\mu\text{m})$  for different applications. The subcell 110 can be formed from a beginning silicon substrate on which the rest of the cell 100 is grown by MBE or otherwise formed. This fabrication methodology may be employed for each of the embodiments illustrated herein. A second subcell 112, which is formed over the first subcell 110, to be in optical communication therewith, and in this embodiment with a tunnel junction 111 between the two, is made of a second material system, comprising a second (p)CdTe base layer 106 and a second (n+)CdTe emitter layer 107 respectively having a second base energy gap ( $E_{g2B} \approx 1.51$ eV), a second emitter energy gap ( $E_{g2E} \approx 1.51$  eV), and a second layer thickness (d<sub>2</sub>≈0.5 to 15 µm, more preferably 2-6 μm). The degenerately alloyed first tunnel junction 111 between the first subcell 110 and second subcell 112 comprises a first (p++)ZnTe base layer 104 and a first (n++)ZnTe emitter layer 105 having a base energy gap ( $E_{gTJE}\approx 2.26$  eV) and an emitter energy gap ( $E_{gTJE}\approx 2.26$  eV) which are relatively high in comparison with the energy gaps of the adjoining layers. The first tunnel junction is made of relatively thin semiconductor layers ( $d_{TJ1}\approx 0.005$  to  $0.1\,\mu m$ ) in order to minimize the absorption of incident light within the tunnel junction and hence reduce optical power loss.

[0047] In this first embodiment of the invention, the material system that is used for the first tunnel junction 111 is not limited to ZnTe semiconductors, but can be made from other relatively high energy gap materials such as CdS (E<sub>gCdS</sub>≈2.46 eV), ZnSe ( $E_{gZnSe} \approx 2.72$  eV), MgTe ( $E_{gMgTe} \approx 3.40$  eV), ZnS ( $E_{gZnS} \approx 3.73$  eV), CdZnTe ( $E_{gCdZnTe} \approx 1.8$  to 2.26 eV), CdMgTe ( $E_{gCdMnTe} \approx 1.8$  to 3.3 eV), CdMnTe ( $E_{gCdMnTe} \approx 1.8$ to 2.92 eV), and ZnMnSe ( $E_{gZnMnSe} \approx 2.8$  to 3.30 eV) compound semiconductors. The energy gaps  $(E_{gTJ1B}$  and  $E_{gTJ1E})$ of the first tunnel junction 111 must be greater than those of the first emitter 103 ( $E_{g1E}$ ) of the first subcell 110 and the second base 106 ( $E_{g2B}$ ) of the second subcell 112. In addition, the (p++) and (n++) tunnel junction with homo-interface (homojunction) can be replaced by a tunnel junction with a hetero-interface (heterojunction) that comprises thin layers semiconductor material having different energy gaps. The first tunnel junction is designed in such a way that the tunneling current density  $(I_{TJ1})$  at the valley is greater than the overall short-circuit photocurrent density (Isc) of the twojunction photovoltaic solar cell 100 in order to minimize the electrical power loss at the interfaces between the first subcell 110, first tunnel junction 111, and second subcell 112.

[0048] An antireflective coating 108, such as a highly transparent thin ZnO semiconductor layer, is formed over (here, immediately adjoining) the second subcell 112 to minimize surface reflections, thereby enabling more photons of the incident light to enter the photovoltaic solar cell, and it is also used as an encapsulant for radiation hardening to improve radiation tolerance against damage from high energy photons and charged particles. The antireflective layer 108 has a relatively wide energy gap ( $E_{gARC} \approx 3.20 \text{ eV}$ ) in comparison to the energy gap of the subcells 110 and 112 that it is protecting, and a relatively thin layer thickness ( $d_{ARC} \approx 0.05$  to  $0.5 \, \mu m$ ). In this first preferred embodiment of the present invention, the antireflective coating 108 is not limited to ZnO semiconductor thin layer, and the antireflection coating can also be made from other materials such as  $Cd_2SnO_4$  ( $E_{gCd2SnO4} \approx 3.07 \text{ eV}$ ),  $SnO_2$  ( $E_{gSnO2} \approx 4.01 \text{ eV}$ ), ZnSe ( $E_{gZnSe} \approx 2.72 \text{ eV}$ ),  $TiO_2$  ( $E_{gTnO2} \approx 3.30 \text{ eV}$ ), MgTe ( $E_{gMgTe} \approx 3.40 \text{ eV}$ ), ZnSe ( $E_{gZnSe} \approx 3.73 \text{ eV}$ ), ZnSe ( $E_{gMgSe} \approx 4.00 \text{ eV}$ ), ZnSe (ZnSe (ZnSe ZnSe Zaddition, the antireflection coating 108 can be made by stacking together multiple thin layers of appropriate thicknesses from the materials described above to further reduce the reflection of the incident light at the top surfaces.

[0049] A back contact 101 can be made from metals for good ohmic contacts such as CoSi<sub>2</sub>, TiSi<sub>2</sub>, WSi<sub>2</sub>, TaSi<sub>2</sub>, PtSi, and Al, and may be made of a metal grid, metal thin layer, or a semi-transparent conducting thin layer. A front contact 109, formed over subcells 110 and 112 in opposition to the back contact 101, is in this embodiment deposited or grown on the antireflection coating 108, can be made from metals such as Au and Cu or transparent conductive oxides (TCOs) such as Cd<sub>2</sub>SnO<sub>4</sub>, SnO<sub>2</sub>, ZnO, and indium tin oxide, and may be a metal grid or a TCO thin layer.

[0050] In this first embodiment of the invention, light that is incident on the top surface of the two-junction photovoltaic solar cell 100 is partially reflected and partially transmitted through the contact layer 109 and the antireflection coating **108**. The transmitted photons with energies  $(E_{ph}>E_{g2B})$  equal to or greater than the second base energy gap of the second subcell 112 are absorbed in the second subcell 112, producing a second short-circuit photocurrent density  $(I_{sc2})$  and a second open-circuit photovoltage  $(V_{oc2})$ . The photons with energies  $(E_{ph} < E_{g2B})$  less than the second base energy gap of the second subcell 112 pass through the second subcell 112 and the first tunnel junction 111, arriving at the top of the first subcell 110. The transmitted photons with energies  $(E_{ph} \ge E_{g1B})$  equal to or greater than the first base energy gap of the first subcell 110 are absorbed in the first subcell 110, producing a first short-circuit photocurrent density  $(I_{sc1})$  and a first open-circuit photovoltage  $(V_{oc1})$ . The layer thicknesses of the first subcell 110 and second subcell 112 are preferably chosen, varied and optimized so that the first short-circuit photocurrent density for the first subcell 110 and second short-circuit photocurrent density for the second subcell 112 are matched completely  $(I_{sc1}=I_{sc2})$  or substantially

[0051] In specific examples of the invention, the short-circuit photocurrent densities, open-circuit voltages, and energy conversion efficiencies of each subcell were calculated using numerical modeling via a finite element method (FEM). In order to compare the upper limit performance of photovoltaic solar cell devices with different architectures, ideal operating conditions were used in the numerical simulations presented herein unless explicitly stated otherwise.

[0052] In the following specific examples, the calculations were based on the solar spectral irradiance of 500 suns at air mass 1.5 with global 37° tilt (AM1.5G) under ideal operating conditions wherein the losses due to scattering, series resistance, optical reflection and absorption, and electrical collection were assumed to be negligible. The calculated first opencircuit voltage  $(V_{oc1})$  for the first subcell 110 and second open-circuit voltage  $(V_{oc2})$  for the second subcell 112 are 0.56 V and 1.09 V, respectively, and the estimated opencircuit voltage for the two-junction photovoltaic solar cell 100 ( $V_{oc} = V_{oc1} + V_{oc2}$ ) is  $\approx 1.65$  V. The calculated optimal first short-circuit photocurrent density  $(I_{sc1})$  for the first subcell 110 and second short-circuit photocurrent density  $(I_{sc2})$  for the second subcell 112 are 40 mA/cm<sup>2</sup> and 27 mA/cm<sup>2</sup>, respectively. From these calculations, the estimated seriesmatched short-circuit photocurrent density  $(I_{sc})$  for the twojunction photovoltaic solar cell 100 is approximately 27  $\text{mA/cm}^2$ , and  $I_{sc}=I_{TJ1}=I_{sc1}=I_{sc2}$  as discussed above. The estimated ideal series-interconnected efficiencies for the first subcell 110  $(\eta_1)$  and second subcell 112  $(\eta_2)$  are 13% and 27%, respectively, and the estimated ideal series-interconnected efficiency  $(\eta = \eta_1 + \eta_2)$  for the two-junction photovoltaic solar cell 100 is approximately 40% under concentrated sunlight.

[0053] In one variation of the first embodiment, the first subcell 110 and second subcell 112 of this homo-junction photovoltaic solar cell 100 can be replaced with hetero-junction subcells to further improve performance by minimizing the absorption in the first emitter 103 and second emitter 107 while maximizing the absorption in the first base 102 of first subcell 110 and second base 106 of the second subcell 112. The first base formed of a semiconductor layer may be Si, Ge, or an SiGe mixture or alloy, and the second CdTe semicon-

ductor base **106** ( $\approx$ 1.51 eV) may be replaced with alloys of CdSe, CdSeTe ( $E_{g1E}$ =1.51 to 1.7 eV), CdZnTe ( $E_{g1E}$ =1.51 to 2.0 eV), CdMgTe ( $E_{g1E}$ =1.51 to 2.0 eV), or CdHgTe ( $E_{g1E}$ =1.3 to 1.6 eV) semiconductors.

[0054] The first (n+)Si emitter 103 of the first subcell 110 can be replaced with alloys of a (n+) Ge emitter ( $E_{g1E}\approx 0.66$  eV), (n+)CdTe emitter ( $E_{g1E}\approx 1.51$  eV), (n+)CdSe emitter ( $E_{g1E}\approx 1.70$  eV), (n+)ZnTe emitter ( $E_{g1E}\approx 2.26$  eV), (n+)CdMnTe emitter ( $E_{g1E}\approx 1.51$  to 2.92 eV), (n+) CdHgTe emitter ( $E_{g1E}\approx 1.3$  to 1.6 eV), (n+)CdSeTe emitter ( $E_{g1E}\approx 1.51$  to 1.70 eV), (n+)CdZnTe emitter ( $E_{g1E}\approx 1.51$  to 2.26 eV), or (n+) CdMgTe emitter ( $E_{g1E}\approx 1.51$  to 3.2 eV) to allow more incident light to reach the first (p-)Si base 102 ( $E_{g1E}\approx 1.10$  eV) in order to increase the photo-generation of electron-hole pairs and hence increase the photocurrent of the first subcell 110.

[0055] In addition, the second (n+)CdTe emitter 107 of the second subcell 112 can be replaced with alloys of a higher energy gap (n+)CdSe emitter ( $E_{g2E}\approx1.70$  eV), (n+)ZnTe emitter ( $E_{g2E}\approx2.26$  eV), (n+)CdS emitter ( $E_{g2E}\approx2.46$  eV), (n+)ZnSe emitter ( $E_{g2E}\approx2.72$  eV), (n+) MgTe emitter ( $E_{g2E}\approx3.40$  eV), (n+)ZnS emitter ( $E_{g2E}\approx3.73$  eV), (n+)CdSeTe emitter ( $E_{g2E}\approx1.51$  to 1.70 eV), (n+)CdZnTe emitter ( $E_{g2E}\approx1.51$  to 2.26 eV), (n+)CdMnTe emitter ( $E_{g2E}\approx1.51$  to 2.26 eV), (n+)CdMnTe emitter (2.26 eV) to allow more incident light to reach the (p-)CdTe base 106 (2.26 eV) in order to increase the photo-generation of electron-hole pairs and hence increase the photocurrent of the second subcell 112.

[0056] Specifically, numerical modeling was performed for a hetero-interface two-junction photovoltaic solar cell: ARC 108=(n+)ZnO; second subcell 112=(n+)ZnTe/(p-)CdTe; tunnel junction 111=(p<sup>+-</sup>)MgTe/(n<sup>++</sup>)MgTe; first subcell 110=(n+)ZnTe/(p)Si. The calculated first open-circuit photovoltage (Voc1) for the first subcell 110 and second opencircuit photovoltage  $(V_{oc2})$  for the second subcell 112 are  $\approx$ 0.56 V and  $\approx$ 1.08 V, respectively. The estimated open-circuit voltage for the thus-specified hetero-interface two-junction photovoltaic solar cell 100 ( $V_{oc}=V_{oc1}+V_{oc2}$ ) is  $\approx 1.64$  V. The calculated optimal first short-circuit photocurrent density  $(I_{sc1})$  for the first subcell 110 and second short-circuit photocurrent density  $(I_{sc2})$  for the second subcell 112 are  $\approx$ 40 mA/cm<sup>2</sup> and ≈29 mA/cm<sup>2</sup>, respectively. The estimated seriesmatched short-circuit photocurrent density (I<sub>sc</sub>) for the hetero-interface two-junction photovoltaic solar cell 100 is approximately 29 mA/cm<sup>2</sup>, and  $I_{sc}=I_{TJ1}=I_{sc1}=I_{sc2}$  as discussed above. The estimated ideal series-interconnected efficiencies for the first subcell 110  $(\eta_1)$  and second subcell 112  $(\eta_2)$  are 14% and 29%, respectively, and the estimated ideal series-interconnected efficiency  $(\eta = \eta_1 + \eta_2)$  for the entire hetero-interface two-junction photovoltaic solar cell 100 is at least  $\approx 43\%$  under 500 suns. In this example, a first  $(p^{++})$ MgTe/(n<sup>-+</sup>) MgTe tunnel junction 111 is placed between the first subcell 110 and second subcell 112. The antireflection coating 108, which may comprise more than one thin layers, can be made of materials with energy gaps that are greater than the energy gap of the second emitter 107 of the second subcell **112** ( $\mathbb{E}_{gARC} > \mathbb{E}_{g2E}$ ).

[0057] The embodiment shown in FIG. 2 is an (n+)ZnO/(n+)CdTe/(p-)CdTe/(n+)Si/(p-)Si two-junction photovoltaic solar cell 200 without a tunnel junction between the subcells 208, 209. In this example, the first subcell 208, which is made of a first material system, comprises a first (p-)Si base layer 202 and a first (n+)Si emitter layer 203 having a first base energy gap ( $E_{elB}\approx 1.10 \text{ eV}$ ), a first emitter energy gap

 $(E_{g1E}\approx 1.10 \, {\rm eV})$ , and a first layer thickness  $(d_1\approx 1.0 \, {\rm to} \, 500 \, \mu {\rm m})$ , more preferably greater than 2  $\mu {\rm m})$ . The second subcell 209, which is formed over, to adjoin or otherwise be in proximate optical communication with the first subcell 208 and which is made of a second material system, comprises a second (p-) CdTe base layer 204 and a second (n+)CdTe emitter layer 205 having a second base energy gap  $(E_{g2E}\approx 1.51 \, {\rm eV})$ , a second emitter energy gap  $(E_{g2E}\approx 1.51 \, {\rm eV})$ , and a second layer thickness  $(d_2\approx 0.5 \, {\rm to} \, 15 \, \mu {\rm m})$ , more preferably greater than 2  $\mu {\rm m})$ . The first subcell 208 and second subcell 209 of this homojunction photovoltaic solar cell 200 can be replaced with hetero-junction subcells as described above to further improve light absorption.

[0058] In a variation of the embodiments illustrated in FIGS. 1 and 2 of the present invention, the conductivity types of the semiconductor layers of the two-junction photovoltaic solar cell are reversed.

[0059] A three-subcell photovoltaic solar cell is schematically illustrated in FIG. 3. This second embodiment encompasses the embodiment shown in FIG. 1 and described above with an additional subcell and preferably a second tunnel junction. The preferred three-subcell photovoltaic solar cell 300  $((n+)ZnO/(n+)Cd_{1-x}Zn_xTe/(p-)Cd_{1-x}Zn_xTe/(p^{++})ZnTe/$  $(n^{++})ZnTe/(n+)CdTe/(p-)CdTe/(p^{++})ZnTe/(n^{++})ZnTe/(n+)$ Si/(p-)Si where the mole fraction x 0.3 1) includes a first subcell 314, a second subcell 316 formed over the subcell 314, a third subcell 318 formed over the second subcell 316, a first tunnel junction 315 interposed between subcells 314 and 316, a second tunnel junction 317 disposed between subcells 316 and 318, an antireflection coating 312, formed above the topmost subcell 318 to provide protection against photons with energies higher than the bandgaps of third subcell 318, a front contact 313, and a back contact 301. The third subcell 314, which is disposed immediately adjacent to the second subcell 316 and is made of a third material system, comprises a third (p-)Cd<sub>1-x</sub>Zn<sub>x</sub>Te base layer 310 and a third (n+)Cd<sub>1-x</sub>Zn<sub>x</sub>Te emitter layer **311** having a third base energy gap ( $E_{g3B} \approx 1.6$  eV-2.0 eV), a third emitter energy gap  $(E_{g3E} \approx 1.6 \text{ eV} - 2.0 \text{ eV})$ , and a third layer thickness  $(d_3 \approx 0.1 \text{ to})$  $10\,\mu m,$  preferably 2 to 6  $\mu m). The degenerately alloyed sec$ ond tunnel junction 317 that is placed between the second subcell 316 and third subcell 318 comprises a second (p<sup>++</sup>) ZnTe base layer 308 and a second (n<sup>++</sup>)ZnTe emitter layer 309 having a relatively high base energy gap (E<sub>gTJ2B</sub>≈2.26 eV) and a relatively high emitter energy gap ( $E_{gTJ2E}$   $\approx$  2.26 eV). In this embodiment, the first tunnel junction 315 and second tunnel junction 317 need not be identical and the tunnel junctions 315, 317 can be made from materials of different energy gaps. The energy gaps  $(E_{gTJ1B}$  and  $E_{gTJ1E})$  of the first tunnel junction 315 must be greater than those of the first emitter 303  $(\mathbf{E}_{\mathbf{g}1E})$  of the first subcell 314 and the second base 306 ( $\mathbb{E}_{g2B}$ ) of the second subcell 316, and the energy gaps  $(E_{gTJ2B}$  and  $E_{gTJ2E})$  of the second tunnel junction 317 must be greater than those of the second emitter 307 ( $E_{e2E}$ ) of the second subcell 316 and the third base 310 ( $E_{g3B}$ ) of the third subcell 318. Specifically, the first and second tunnel junctions may be alloys of ZnTe, ZnS, MgTe, ZnS, CdZnTe (E<sub>gTJ2</sub>≈2.0 to 2.26 eV), and CdMgTe ( $E_{gTJ2}\approx$ 2.0 to 3.2 eV).

[0060] Light that is incident on the top surface of the three-junction photovoltaic solar cell 300 is partially reflected and partially transmitted through the contact layer 313 and the antireflection coating 312. The transmitted photons with energies  $(\mathbb{E}_{ph} \ge \mathbb{E}_{g3B})$  equal to or greater than the third base energy gap of the third subcell 318 are absorbed in the third

subcell 318, producing a third short-circuit photocurrent density  $(I_{sc3})$  and a third open-circuit photovoltage  $(V_{oc3})$ . The photons with energies  $(E_{ph} < E_{g3B})$  less than the energy gap of the third subcell 318 pass through the third subcell 318 and the second tunnel junction 317 impinging on the top of the second subcell 316. The transmitted photons with energies  $(E_{ph} \ge E_{e2B})$  equal to or greater than the second base energy gap of the second subcell 316 are absorbed in the second subcell 316, producing a second short-circuit photocurrent density  $(I_{sc2})$  and a second open-circuit photovoltage  $(V_{ac2})$ . The photons with energies  $(E_{ph} < E_{g2B})$  less than the second base energy gap of the second subcell 316 pass through the second subcell 316 and the first tunnel junction 315 reaching the top of the first subcell 314. The transmitted photons with energies  $(E_{ph} \ge E_{g1B})$  equal to or greater than the first base energy gap of the first subcell 314 are absorbed in the first subcell 314, producing a first short-circuit photocurrent density  $(I_{scl})$  and a first open-circuit photovoltage  $(V_{acl})$ . The thicknesses of the first subcell 315, second subcell 316, and third subcell 318 are chosen and optimized so that the first short-circuit photocurrent density for the first subcell 314, second short-circuit photocurrent density for the second subcell 316, and third short-circuit photocurrent density for the third subcell 318 are matched completely  $(I_{sc1}=I_{sc2}=I_{sc3})$  or substantially  $(I_{sc1} \approx I_{sc2} \approx I_{sc3})$ .

[0061] In a specific example of this three-subcell embodiment, the calculated first open-circuit photovoltage  $(V_{oc1})$  for the first subcell 314, second open-circuit photovoltage  $(V_{oc2})$ for the second subcell 316, and third open-circuit photovoltage  $(V_{ac3})$  for the third subcell 318 are  $\approx 0.53 \text{ V}, \approx 0.97 \text{ V}$ , and ≈1.26 V, respectively. The estimated open-circuit photovoltage for the three-subcell photovoltaic solar cell 300 $({\rm V}_{oc}\!\!=\!\!{\rm V}_{oc1}\!\!+\!\!{\rm V}_{oc2}\!\!+\!\!{\rm V}_{oc3})$  is  ${\bf 2.76}\,\rm V$  . The calculated optimal first short-circuit photocurrent density  $(I_{sc1})$  for the first subcell 314, second short-circuit photocurrent photocurrent density  $(I_{sc2})$  for the second subcell 316, and third short-circuit density ( $I_{sc3}$ ) for third subcell 318 are  $\approx$ 40 mA/cm<sup>2</sup>,  $\approx$ 27 mA/cm<sup>2</sup>, and ≈19 mA/cm<sup>2</sup>, respectively. From these numerical calculations, the estimated series-matched short-circuit photocurrent density (I<sub>sc</sub>) for the three-junction photovoltaic solar cell 300 under concentrated sunlight (500 suns) is approximately 19 mA/cm<sup>2</sup>, and  $I_{sc} = I_{TJ1} = I_{TJ2} = I_{sc1} = I_{sc2} = I_{sc3}$  as discussed above. The estimated ideal series-interconnected efficiency  $(\eta = \eta_1 + \eta_2 + \eta_3)$  for the three-junction photovoltaic solar cell 300 is at least ≈40%. As described previously, degeneratively alloyed (p<sup>++</sup>)ZnTe/(n<sup>++</sup>)ZnTe tunnel junctions 315, 317 may placed between the subcells to improve the light conversion efficiency for cell 300.

[0062] Alternatively, the first subcell 314, second subcell 316, and third subcell 318 of this homo-junction photovoltaic solar cell 300 can be replaced with hetero-junction subcells to further improve performance by minimizing the absorption in the first emitter 303 of the first subcell 314, second emitter 307 of the second subcell 316 and third emitter 311 of the third subcell 318, while maximizing the absorption in the first base 302 of first subcell 314, second base 306 of the second subcell 316, and third base 310 of the third subcell 318.

[0063] Additionally, the (n+)Cd<sub>1-x</sub>Zn<sub>x</sub>Te emitter 311 of the third subcell 318 can be replaced with alloys of a higher energy gap (n+)CdSe emitter ( $E_{g3E}$ =1.70 eV), (n+)ZnTe emitter ( $E_{g3E}$ =2.26 eV), (n+)CdS emitter ( $E_{g3E}$ =2.46 eV), (n+)ZnSe emitter ( $E_{g3E}$ =2.72 eV), (n+)MgTe emitter ( $E_{g3E}$ =3.40 eV), (n+)ZnS emitter ( $E_{g3E}$ =3.73 eV), (n+)CdZnTe emitter ( $E_{g3E}$ =1.6 to 2.26 eV), (n+)CdMnTe emitter

 $(E_{g3E}\approx 1.6 \text{ to } 3.2 \text{ eV}), (n+)\text{CdSeTe}$  emitter  $(E_{g3E}\approx 1.6 \text{ to } 1.7 \text{ eV}), \text{ or } (n+)\text{CdMgTe}$  emitter  $(E_{g3E}\approx 1.6 \text{ to } 3.2 \text{ eV})$  to allow more incident light to reach the  $(p)\text{Cd}_{1-x}Zn_x\text{Te}$  base **310**  $(E_{g3B}\approx 1.71 \text{ eV})$  in order to increase the photo-generation of electron-hole pairs and hence increase the photocurrent of the third subcell **318**.

[0064] The third CdZnTe base 310 ( $\rm E_{g3B}{\approx}1.6$  to 2.0 eV) may be replaced with alloys of CdSeTe ( $\rm E_{g3B}{=}1.6$  to 1.7 eV), CdZnTe ( $\rm E_{g3B}{=}1.6$  to 2.0 eV), or CdMgTe ( $\rm E_{g3B}{=}1.6$  to 2.0 eV) semiconductors.

[0065] Modeling was performed for a hetero-interface three-junction photovoltaic solar cell having the following top-to-bottom composition: (n+)ZnO/(n+)ZnTe/(p-)Cd<sub>1-</sub>  $_xZn_xTe/(p^{++})MgTe/(n^{++})MgTe/(n+)ZnTe/(p-)CdTe/(p^{++})$  $MgTe/(n^{++})MgTe/(n^{+})ZnTe/(p-)Si$ . The calculated first open-circuit photovoltage  $(V_{ocl})$  for the first subcell 314, second open-circuit photovoltage  $(V_{oc2})$  for the second subcell 316, and third open-circuit photovoltage  $(V_{oc3})$  for the third subcell 318 were ≈0.54 V, ≈0.97 V, and ≈1.26 V, respectively. The estimated open-circuit voltage for the hetero-interface three-subcell photovoltaic solar cell 300 ( $V_{oc} = V_{oc1} +$  $V_{oc2}+V_{oc3}$ ) was  $\approx 2.77$  V. The calculated optimal first shortcircuit photocurrent density  $(I_{sc1})$  for the first subcell 314, second short-circuit photocurrent density  $(I_{so2})$  for the second subcell **316**, and third short-circuit photocurrent density  $(I_{sc3})$ for the third subcell 318 were  $\approx 40 \text{ mA/cm}^2$ ,  $\approx 27 \text{ mA/cm}^2$ , and ≈21 mA/cm<sup>2</sup>, respectively. In this case, the estimated seriesmatched short-circuit photocurrent density (I<sub>sc</sub>) for the threejunction photovoltaic solar cell 300 was approximately 21  $\text{mA/cm}^2$ , and  $I_{sc} = I_{TJ1} = I_{TJ2} = I_{sc1} = I_{sc2} = I_{sc3}$  as discussed above. The estimated ideal series-interconnected efficiencies for the first subcell 314  $(\eta_1)$ , second subcell 316  $(\eta_2)$ , and third subcell 318 ( $\eta_3$ ) are 10%, 18%, and 24%, respectively, and the estimated ideal series-interconnected efficiency ( $\eta = \eta_1 +$  $\eta_2 + \eta_3$ ) for the hetero-interface three-junction photovoltaic solar cell 300 was ≈52% under 500 suns. In this example, (p<sup>++</sup>)MgTe/(n<sup>++</sup>) MgTe tunnel junctions were placed between subcells to improve light conversion efficiency. The antireflection coating 312, which may comprise more than one thin layer, can be made of materials with energy gaps that are greater than the energy gap of the emitter 311 of the third subcell 318 ( $E_{gARC} > E_{g3E}$ ). For instance, the antireflection coating may be made of Cd<sub>2</sub>SnO<sub>4</sub>, SnO<sub>2</sub>, ZnSe, TiO<sub>2</sub>, MgTe, ZnO, ZnS, MgSe, ITO, MgS, MgO, SiO<sub>2</sub>, and MgF<sub>2</sub> semiconductors.

[0066] FIG. 4 illustrates a three-subcell photovoltaic solar cell 400 without intervening tunnel junctions. A representative composition is, top-to-bottom, (n+)ZnO/(n+)Cd<sub>1-</sub>  $_x$ Zn $_x$ Te/(p-)Cd $_{1-x}$ Zn $_x$ Te/(n+)CdTe/(p-)CdTe/(n+)Si/(p-)Si. In this example, the first subcell 410, which is made of a first, preferably Group IV material system, comprises a first (p-)Si base layer 402 and a first (n+)Si emitter layer 403 having a first base energy gap ( $E_{g1E}$ =1.10 eV), a first emitter energy gap (E<sub>g1E</sub>26 1.10 eV), and a first layer thickness (d<sub>1</sub>≈1.0 to 500  $\mu$ m, preferably greater than or equal to 2  $\mu$ m). The second subcell 411, which is disposed immediately adjacent to the first subcell 410 and is made of a second, preferably Group II-VI material system, comprises a second (p-)CdTe base layer 404 and a second (n+)CdTe emitter layer 405 having a second base energy gap ( $E_{g2B}\approx1.51$  eV), a second emitter energy gap ( $E_{g2E}\approx1.51$  eV), and a second layer thickness  $(d_2 \approx 0.5 \text{ to } 15 \text{ } \mu\text{m})$ . A third subcell **412**, which is disposed immediately adjacent to the second subcell 411 and is made of a third, preferably Group II-VI material system, comprises

a third  $(p-)Cd_{1-x}Zn_x$ Te base layer **406** and a third  $(n+)Cd_{1-x}Zn_x$ Te emitter layer **407** having a third base energy gap  $(E_{g3B}\approx 1.71 \text{ eV})$ , a third emitter energy gap  $(E_{g3B}\approx 1.71 \text{ eV})$ , and a third layer thickness  $(d_3\approx 0.1 \text{ to } 10 \text{ µm})$ , preferably 2-6 µm). The first subcell **410**, second subcell **411** and third subcell **412** of this homo-junction photovoltaic solar cell **400** can be replaced with hetero-junction subcells as described above to further improve incident light absorption.

[0067] In another variation of the second embodiment of the present invention, the (p-) and (n) semiconductor layers of the three-junction photovoltaic solar cell are reversed.

[0068] In another embodiment of the present invention, the important features of a four-subcell photovoltaic solar cell are schematically illustrated in FIG. 5. This embodiment adds to the embodiment shown in FIG. 3 with an additional subcell and tunnel junction. The composition of a preferred foursubcell photovoltaic solar cell 500 is, from top-to-bottom,  $(n+)ZnO/(n+)Cd_{1-\nu}Zn_{\nu}Te/(p-)Cd_{1-\nu}Zn_{\nu}Te/(p^{++})ZnTe/(n^{++})$  $ZnTe/(n+)Cd_{1-x}Zn_xTe/(p-)Cd_{1-x}Zn_xTe/(p^{++})ZnTe/(n^{++})$  $ZnTe/(n+)CdTe/(p-)CdTe/(p^{++})ZnTe/(n^{++})ZnTe/(n+)Si/(p-)$ Si, where the mole fraction  $x\approx0.31$  and  $y\approx0.58$ . Cell 500 includes a first subcell 518, a second subcell 520, a third subcell 522, a fourth subcell 524, a first tunnel junction 519 between subcells 518 and 520, a second tunnel junction 521 between subcells 520 and 522, a third tunnel junction 523 between subcells 522 and 524, an antireflection coating 516 disposed over the topmost subcell 522, a front contact 517, and a back contact 501.

[0069] The fourth subcell 524, which is disposed over and in optical communication with the third subcell 522, is made of a fourth, preferably Group II-VI material system, more preferably comprising a fourth  $(p-)Cd_{1-y}Zn_yTe$  base layer 514 and a fourth  $(n+)Cd_{1-y}Zn_yTe$  emitter layer 515 having a fourth base energy gap  $(E_{gAE}=1.7 \text{ to } 2.0 \text{ eV})$ , a fourth emitter energy gap  $(E_{gAE}=1.8 \text{ to } 2.26 \text{ eV})$ , and a fourth layer thickness  $(d_a=0.1 \text{ to } 10 \text{ µm})$ , preferably 2-6  $\mu$ m).

[0070] The degenerately alloyed third tunnel junction 523 that is placed between the third subcell **522** and fourth subcell 524 preferably comprises a third (p++)ZnTe base layer 512 and a third (n++) ZnTe emitter layer 513 having a relatively high base energy gap ( $E_{gTJ3B}\approx 2.26 \text{ eV}$ ) and a relatively high emitter energy gap ( $E_{gTJ3E}\approx 2.26 \text{ eV}$ ). The first tunnel junction tion 519, second tunnel junction 521, and third second tunnel junction 523 need not be identical and the tunnel junctions 519, 521, and 523 can be made from materials of different energy gaps. The energy gaps  $(\mathbf{E}_{gTJ1B}$  and  $\mathbf{E}_{gTJ1E})$  of the first tunnel junction 519 must be greater than those of the first emitter **503** ( $\mathbf{E}_{g1E}$ ) of the first subcell **518** and the second base **506** ( $\mathbf{E}_{g2B}$ ) of the second subcell **520**; the energy gaps ( $\mathbf{E}_{gTJ2B}$ and  $E_{gTJ2E}$ ) of the second tunnel junction **521** must be greater than those of the second emitter 507  $(E_{g2E})$  of the second subcell 520 and the third base 510 ( $E_{g3B}$ ) of the third subcell **522**; the energy gaps  $(E_{gTJ3B}$  and  $E_{gTJ3E})$  of the third tunnel junction 523 must be greater than those of the third emitter 511 ( $E_{g3E}$ ) of the third subcell 522 and the fourth base 514  $(E_{g4B})$  of the fourth subcell **524**. The first, second, and third tunnel junctions may be one or more layers of at least one alloy of ZnTe, ZnS, ZnO, MgTe, CdMnTe ( $\mathbb{E}_{gTJ3}$  2.0 to 2.92 eV), CdZnTe ( $E_{gTJ3}$  2.0 to 2.26 eV), and CdMgTe ( $E_{gTJ3}$  2.0

[0071] In this embodiment light that is incident on the top surface of the four-subcell photovoltaic solar cell 500 is partially reflected and partially transmitted through the contact layer 517 and the antireflection coating 516. The transmitted

photons with energies  $(E_{ph} \ge E_{g4B})$  equal to or greater than the fourth base energy gap of the fourth subcell 524 are absorbed in the fourth subcell 524, producing a fourth short-circuit photocurrent density (I<sub>sc4</sub>) and a fourth open-circuit photovoltage  $(V_{oc4})$ . The photons with energies  $(E_{ph} < E_{g4B})$  less than the fourth base energy gap of the fourth subcell 524 pass through the fourth subcell 524 and the third tunnel junction 523 impinging on the top of the third subcell 522. The transmitted photons with energies  $(E_{ph} \ge E_{g3B})$  equal to or greater than the third base energy gap of the third subcell 522 are absorbed in the third subcell 522, producing a third shortcircuit photocurrent density  $(I_{sc3})$  and a third open-circuit photovoltage  $(V_{oc3})$ . The photons with energies  $(E_{ph} < E_{g3B})$ less than the third base energy gap of the third subcell 522 pass through the third subcell 522 and the second tunnel junction 521, reaching the top of the second subcell 520.

[0072] The transmitted photons with energies  $(E_{nh} \ge E_{o2B})$ equal to or greater than the second base energy gap of the second subcell 520 are absorbed in the second subcell 520, producing a second short-circuit photocurrent density  $(I_{sc2})$ and a second open-circuit photovoltage  $(V_{oc2})$ . The photons with energies  $(E_{ph} < E_{g2B})$  less than the second base energy gap of the second subcell **520** pass through the second subcell 520 and the first tunnel junction 519, arriving at the top of the first subcell 518. The transmitted photons with energies  $(E_{ph} \ge E_{g1B})$  equal to or greater than the first base energy gap of the first subcell 518 are absorbed in the first subcell 518, producing a first short-circuit photocurrent density (I<sub>sc1</sub>) and a first open-circuit photovoltage  $(V_{oc1})$ . The thicknesses of the first subcell 518, second subcell 520, third subcell 522, and fourth subcell 524 are chosen and optimized so that the first short-circuit photocurrent density for the first subcell 518, second short-circuit photocurrent density for the second subcell 520, third short-circuit photocurrent density for the third subcell 522, and fourth short-circuit photocurrent density for the fourth subcell 524 are matched completely  $(\mathbf{I}_{sc1} = \mathbf{I}_{sc2} = \mathbf{I}_{sc3} = \mathbf{I}_{sc4}) \text{ or substantially } (\mathbf{I}_{sc1} \approx \mathbf{I}_{sc2} \approx \mathbf{I}_{sc3} \approx \mathbf{I}_{sc4})$ 

[0073] In a specific example of this embodiment, the calculated first open-circuit photovoltage  $(V_{oc1})$  for the first subcell 518, second open-circuit photovoltage  $(V_{oc2})$  for the second subcell 520, third open-circuit photovoltage  $(V_{oc3})$  for the third subcell 522, and fourth open-circuit photovoltage  $(V_{oc4})$  for the fourth subcell 524 were  $\approx 0.51 \, \text{V}, \approx 0.91 \, \text{V}, \approx 1.15 \, \text{V}$ , and  $\approx 1.44 \, \text{V}$ , respectively. The estimated open-circuit voltage for the four-junction photovoltaic solar cell 500  $(V_{oc} = V_{oc1} + V_{oc2} + V_{oc3} + V_{oc4})$  was  $\approx 4.01 \, \text{V}$ .

[0074] The calculated optimal first short-circuit photocurrent density ( $I_{sc1}$ ) for the first subcell 518, second short-circuit photocurrent density ( $I_{sc2}$ ) for the second subcell 520, third short-circuit photocurrent density ( $I_{sc3}$ ) for the third subcell 522, and fourth short-circuit photocurrent density ( $I_{sc4}$ ) for the fourth subcell 524 were ≈40 mA/cm², ≈27 mA/cm², ≈19 mA/cm², and ≈15 mA/cm², respectively. From these numerical calculations, the estimated series-matched current density ( $I_{sc}$ ) for the four-junction photovoltaic solar cell 500 was approximately 15 mA/cm², and  $I_{sc}=I_{LT}=I_{LT2}=I_{LT3}=I_{sc1}=I_{sc2}=I_{sc3}=I_{sc4}$  as discussed above.

[0075] The estimated ideal series-interconnected efficiency  $(\eta = \eta_1 + \eta_2 + \eta_3 + \eta_4)$  for the four-junction photovoltaic solar cell 500 was at least  $\approx$ 45% under 500 suns. As described in the second embodiment of the present invention,  $(p^{++})ZnTe/(n^{++})$  ZnTe tunnel junctions were placed between the subcells to improve the light conversion efficiency.

[0076] The first subcell 518, second subcell 520, third subcell 522, and fourth subcell 524 of this homo-junction photovoltaic solar cell 500 illustrated in FIG. 5 can be replaced with hetero-junction subcells to further improve performance by minimizing the absorption in the first emitter 518, second emitter 520, third emitter 522, and fourth emitter 524 while maximizing the absorption in the first base 502 of the first subcell 518, second base 506 of the second subcell 520, third base 510 of the third subcell 522, and fourth base 514 of the fourth subcell 524.

[0077] Furthermore, the fourth (n+)Cd<sub>1-y</sub>Zn<sub>y</sub>Te emitter 515 of the fourth subcell 524 can be replaced by alloys with a higher energy gap (n+)ZnTe emitter ( $E_{g4E}\approx2.26$  eV), (n+)CdS emitter ( $E_{g4E}\approx2.46$  eV), (n+)ZnSe emitter ( $E_{g4E}\approx2.72$  eV), (n+)MgTe emitter ( $E_{g4E}\approx3.40$  eV), (n+)ZnS emitter ( $E_{g4E}\approx3.73$  eV), (n+)CdZnTe emitter ( $E_{g4E}\approx1.8$  to 2.26 eV), (n+)CdMnTe emitter ( $E_{g4E}\approx1.8$  to 3.0 eV), or (n+)CdMgTe emitter ( $E_{g4E}\approx1.80$  to 3.2 eV) to allow more incident light to reach the (p-)Cd<sub>1-y</sub>Zn<sub>y</sub>Te base 514 ( $E_{g4E}\approx1.91$  eV) in order to increase the photo-generation of electron-hole pairs and hence increase the photocurrent of the fourth subcell 524.

**[0078]** The fourth semiconductor base material may be alloys of a CdZnTe ( $\rm E_{\it g4B}$  1.7 to 2.0 eV) semiconductor or a CdMgTe ( $\rm E_{\it g4B}$  1.7 to 2.0 eV) semiconductor.

[0079] Modeling was performed for a hetero-interface four-junction photovoltaic solar cell having the following top-to-bottom composition: (n+)ZnO/(n+)ZnTe/(p-)Cd<sub>1-y</sub>Zn<sub>y</sub>Te/(p<sup>++</sup>)MgTe/(n+)ZnTe/(p-)CdTe/(p<sup>++</sup>)MgTe/(n+)MgTe/(n+)ZnTe/(p-)CdTe/(p<sup>++</sup>)MgTe/(n+)MgTe/(n+)ZnTe/(p-)Si. The calculated first open-circuit photovoltage (V<sub>oc1</sub>) for the first subcell **518**, second open-circuit photovoltage (V<sub>oc2</sub>) for the second subcell **520**, third open-circuit photovoltage (V<sub>oc3</sub>) for the third subcell **522**, and fourth open-circuit photovoltage (V<sub>oc4</sub>) for the fourth subcell **524** were  $\approx$ 0.52 V,  $\approx$ 0.93 V,  $\approx$ 1.18 V, and  $\approx$ 1.44 V, respectively. The estimated open-circuit voltage for the four-junction photovoltaic solar cell **500** (V<sub>oc</sub>=V<sub>oc1</sub>+V<sub>oc2</sub>+V<sub>oc3</sub>+V<sub>oc4</sub>) was  $\approx$ 4.07 V.

[0080] The calculated optimal first short-circuit photocurrent density ( $I_{sc1}$ ) for the first subcell **518**, second short-circuit photocurrent density ( $I_{sc2}$ ) for the second subcell **520**, third short-circuit photocurrent density ( $I_{sc3}$ ) for the third subcell **522**, and fourth short-circuit photocurrent density ( $I_{sc4}$ ) for the fourth subcell **524** were ≈40 mA/cm², ≈27 mA/cm², ≈21 mA/cm², and ≈16 mA/cm², respectively. In this case, the estimated series-matched short-circuit photocurrent density ( $I_{sc}$ ) for the hetero-interface four-junction photovoltaic solar cell **500** was approximately 16 mA/cm², and  $I_{sc}=I_{TJ1}=I_{TJ2}=I_{TJ3}=I_{sc1}=I_{sc2}=I_{sc3}=I_{sc4}$  as discussed above.

[0081] The estimated ideal series-interconnected efficiencies for the first subcell 518  $(\eta_1)$ , second subcell 520  $(\eta_2)$ , third subcell 522  $(\eta_3)$ , and fourth subcell 524  $(\eta_4)$  were 7%, 12%, 18%, and 21%, respectively, and the estimated ideal series-interconnected efficiency  $(\eta = \eta_1 + \eta_2 + \eta_3 + \eta_4)$  for the hetero-interface four-junction photovoltaic solar cell 500 was  $\approx$ 58% under 500 suns. In this particular example,  $(p^{++})$  MgTe/ $(n^{++})$ MgTe tunnel junctions were placed between the subcells to improve light conversion efficiency. The antireflection coating 516, which may comprise more than one thin layer, can be made of materials with energy gaps that are greater than the energy gap of the emitter 515 of the fourth subcell 524  $(E_{gARC} > E_{gAE})$ . For instance, the antireflection coating can be made of (n+)MgTe  $(E_{gARC} \approx 3.40 \text{ eV})$  semiconductor thin layer.

[0082] FIG. 6 shows a four-subcell photovoltaic cell 600 without tunnel junctions. A top-to-bottom composition of cell **600** can be  $(n+)ZnO/(n+)Cd_{1-\nu}Zn_{\nu}Te/(p-)Cd_{1-\nu}Zn_{\nu}Te/(n+)$  $Cd_{1-x}Zn_xTe/(p-)Cd_{1-x}Zn_xTe/(n+)CdTe/(p-)CdTe/(n+)Si/$ (p-)Si. In this example, the first subcell 612, which is made of a first, preferably Group IV material system, more preferably comprises a first (p-)Si base layer 602 and a first (n+)Si emitter layer 603 having a first base energy gap ( $E_{g1B} \approx 1.10$ eV), a first emitter energy gap ( $E_{g1E}\approx 1.10$  eV), and a first layer thickness ( $d_1 \approx 11.0$  to 500  $\mu m$ , preferably at least 2  $\mu m$ ). The second subcell 613, which is disposed immediately adjacent to the first subcell 612 and is made of a second, preferably Group II-VI material system, more preferably comprises a second (p-)CdTe base layer 604 and a second (n+)CdTe emitter layer 605 having a second base energy gap ( $E_{g2B} \approx 1$ . 51 eV), a second emitter energy gap ( $E_{g2E}\approx 1.51$  eV), and a second layer thickness (d<sub>2</sub>≈0.5 to 15 µm, preferably 2 to 6 μm). The third subcell **614**, which is disposed immediately adjacent to the second subcell 613 and is made of a third, preferably Group II-VI material system, more preferably comprises a third  $(p-)Cd_{1-x}Zn_x$ Te base layer **606** and an (n+)Cd<sub>1-x</sub>Zn<sub>x</sub>Te emitter layer 607 having a third energy gap  $(E_{\alpha 3} \approx 1.71 \text{ eV})$  and a third layer thickness  $(d_3 \approx 0.1 \text{ to } 10 \text{ } \mu\text{m})$ preferably 2 to 6 µm). The fourth subcell 615, which is disposed immediately adjacent to the third subcell 614 and is made of a fourth, preferably Group II-VI material system, more preferably comprises a (p-)Cd<sub>1-v</sub>Zn<sub>v</sub>Te base layer **608** and a fourth (n+)Cd<sub>1-y</sub>Zn<sub>v</sub>Te emitter layer 609 having a fourth base energy gap (E<sub>g4B</sub>≈1.91 eV), a fourth emitter energy gap  $(E_{g4E}\approx 1.91 \text{ eV})$ , and a fourth layer thickness  $(d_4\approx 0.1 \text{ to } 10$ μm). The first subcell **612**, second subcell **613**, third subcell **614**, and fourth subcell **615** of the homo-junction photovoltaic solar cell 600 can be replaced with hetero-junction subcells as described above to further improve incident light absorption.

[0083] In another variation of this embodiment, the (p-) and (n) semiconductor layers of the four-subcell photovoltaic solar cell are reversed.

[0084] In another embodiment of the present invention, the main features of a five-junction photovoltaic solar cell are schematically illustrated in FIG. 7. This embodiment adds, to the embodiment shown in FIG. 5, an additional subcell and tunnel junction. A preferred composition of the five-subcell photovoltaic solar cell 700 is, from top to bottom, (n+)ZnO/  $({\rm n+}){\rm Cd}_{1-z}{\rm Zn}_z{\rm Te}/({\rm p-}){\rm Cd}_{1-z}{\rm Zn}_z{\rm Te}/({\rm p^{++}}){\rm ZnTe}/({\rm n^{++}}){\rm ZnTe}/({\rm n+})$  $Cd_{1-y}Zn_{y}Te/(p-)Cd_{1-y}Zn_{y}Te/(p^{++})ZnTe/(n^{++})ZnTe/(n+)C_{1-}$  ${}_{x}Zn_{x}Te/(p-)Cd_{1-x}Zn_{x}Te/(p^{++})ZnTe/(n^{++})ZnTe/(n+)CdTe/(p-)CdTe/(p^{++})ZnTe/(n^{++})ZnTe/(n+)Si/(p-)Si,$  where the mole fraction x≈0.31, y≈0.58, and z≈0.70. Cell 700 includes a first subcell 722, a second subcell 724, a third subcell 726, a fourth subcell 728, a fifth subcell 730, a first tunnel junction 723 between subcells 722 and 724, a second tunnel junction 725 between subcells 724 and 726, a third tunnel junction 727 between subcells 726 and 728, a fourth tunnel junction 729 between subcells 728 and 730, an antireflection coating 720 formed to be disposed over the topmost subcell 730, a front contact 721, and a back contact 701.

[0085] The fifth subcell 730 is disposed over and in optical communication with the fourth subcell 728, and is made of a fifth, preferably II-VI material system, more preferably comprising a fifth  $(p_-)Cd_{1-z}Zn_zTe$  base layer 718 and a fifth  $(n_+)Cd_{1-z}Zn_zTe$  emitter layer 719, having a fifth base energy gap  $(E_{g5B}\approx 2.00 \text{ eV})$ , a fifth emitter energy gap  $(E_{g5B}\approx 2.00 \text{ eV})$ , and a fifth layer thickness  $(d_5\approx 0.1 \text{ to } 10 \text{ µm})$ . The degener-

ately alloyed fourth tunnel junction **729** that is placed between the fourth subcell **728** and fifth subcell **730** preferably comprises a fourth (p<sup>++</sup>)ZnTe base layer **716** and a fourth (n<sup>++</sup>)ZnTe emitter layer **717** having a relatively high base energy gap ( $E_{gTJAB}\approx 2.26$  eV) and a relatively high emitter energy gap ( $E_{gTJAE}\approx 2.26$  eV).

[0086] The first tunnel junction 723, second tunnel junction 725, third tunnel junction 727, and fourth tunnel junction 729 need not be identical and the tunnel junctions 723, 725, 727, 729 can be made from materials of different energy gaps. The energy gaps  $(E_{gTJ1B}$  and  $E_{gTJ1E})$  of the first tunnel junction 723 must be greater than those of the first emitter 703 ( $E_{gE1}$ ) of the first subcell 722 and the second base 706  $(E_{g2B})$  of the second subcell **724**; the energy gaps ( $E_{gTJ2B}$  and  $E_{gTJ2E}$ ) of the second tunnel junction **725** must be greater than those of the second emitter 707 ( $\mathbb{E}_{g2E}$ ) of the second subcell 724 and the third base 710 ( $E_{g3B}$ ) of the third subcell 726; the energy gaps  $(E_{gTJ3B}$  and  $E_{gTJ3E})$  of the third tunnel junction 727 must be greater than those of the third emitter 711 ( $E_{g3E}$ ) of the third subcell **726** and the fourth base **714**  $(\mathbb{E}_{g4B})$  of the fourth subcell 728; and the energy gaps  $(E_{gTJ4B}$  and  $E_{gTJ4E})$  of the fourth tunnel junction 729 must be greater than those of the fourth emitter 715 ( $\mathbf{E}_{g4E}$ ) of the fourth subcell 728 and the fifth base 718 ( $E_{g5B}$ ) of the fifth subcell 730. The first, second, third, and fourth tunnel junctions may be one or more alloyed semiconductor layers of ZnTe, ZnS, MgTe, ZnO, CdZnTe  $(E_{gTJ4} \approx 2.0 \text{ to } 2.26 \text{ eV})$ , CdMgTe  $(E_{gTJ4} \approx 2.0 \text{ to } 3.4 \text{ eV})$ , and CdMnTe ( $E_{gTJ4} \approx 2.0 \text{ to } 2.92 \text{ eV}$ ).

[0087] Light that is incident on the top surface of the fivejunction photovoltaic solar cell 700 is partially reflected and partially transmitted through the contact layer 721 and the antireflection coating 720. The transmitted photons with energies  $(E_{ph} \ge E_{g5B})$  equal to or greater than the fifth base energy gap of the fifth subcell 730 are absorbed in the fifth subcell 730, producing a fifth short-circuit photocurrent density  $(I_{sc5})$  and a fifth open-circuit photovoltage  $(V_{oc5})$ . The photons with energies  $(E_{ph} < E_{g5B})$  less than the fifth base energy gap of the fifth subcell 730 pass through the fifth subcell 730 and the fourth tunnel junction 729, impinging on the top of the fourth subcell 728. The transmitted photons with energies  $(E_{ph} \cong E_{g4B})$  equal to or greater than the fourth base energy gap of the fourth subcell 728 are absorbed in the fourth subcell 728, producing a fourth short-circuit photocurrent density  $(I_{sc4})$  and a fourth open-circuit photovoltage  $(V_{oc4})$ . Photons with energies  $(E_{ph} < E_{g4B})$  less than the fourth base energy gap of the fourth subcell **728** pass through the fourth subcell 728 and the third tunnel junction 727, reaching the top of the third subcell **726**.

[0088] The transmitted photons with energies  $(E_{ph}>E_{g3B})$ equal to or greater than the third base energy gap of the third subcell **726** are absorbed in the third subcell **726**, producing a third short-circuit photocurrent density  $(I_{sc3})$  and a third open-circuit photovoltage ( $V_{oc3}$ ). The photons with energies  $(E_{ph} < E_{g3B})$  less than the third base energy gap of the third subcell 726 pass through the third subcell 726 and the second tunnel junction 725, arriving at the top of the second subcell **724**. The transmitted photons with energies  $(E_{ph}>E_{g2B})$  equal to or greater than the second base energy gap of the second subcell 724 are absorbed in the second subcell 724, producing a second short-circuit photocurrent density  $(I_{sc2})$  and a second open-circuit photovoltage  $(V_{oc2})$ . The photons with energies  $(E_{ph} < E_{g2B})$  less than the second base energy gap of the second subcell 724 pass through the second subcell 724 and the first tunnel junction 723, arriving the top of the first

subcell 722. The transmitted photons with energies  $(E_{ph} \ge E_{g1B})$  equal to or greater than the first base energy gap of the first subcell 722 are absorbed in the first subcell 722, producing a first short-circuit photocurrent density  $(I_{sc1})$  and a first open-circuit photovoltage  $(V_{oc1})$ .

[0089] The thicknesses of the first subcell 722, second subcell 724, third subcell 726, fourth subcell 728, and fifth subcell 730 are varied and optimized so that the first short-circuit photocurrent density ( $I_{sc1}$ ) for the first subcell, second short-circuit photocurrent density ( $I_{sc2}$ ) for the second subcell, third short-circuit photocurrent density ( $I_{sc3}$ ) for the third subcell, fourth short-circuit photocurrent density ( $I_{sc3}$ ) for the fourth subcell, and fifth short-circuit photocurrent density ( $I_{sc5}$ ) for the fifth subcell are matched completely ( $I_{sc1} = I_{sc2} = I_{sc3} = I_{sc4} = I_{sc5}$ ) or substantially ( $I_{sc1} = I_{sc2} = I_{sc3} = I_{sc4} = I_{sc5}$ ).

**[0090]** In a specific example of this embodiment, the calculated first open-circuit photovoltage  $(V_{oc1})$  for the first subcell **722**, second open-circuit photovoltage  $(V_{oc2})$  for the second subcell **724**, third open-circuit voltage  $(V_{oc3})$  for the third subcell **726**, fourth open-circuit photovoltage  $(V_{oc4})$  for the fourth subcell **728**, and fifth open-circuit photovoltage  $(V_{oc5})$  for the fifth subcell **730** were  $\approx$ 0.50 V,  $\approx$ 0.90 V,  $\approx$ 1.12 V,  $\approx$ 1.36 V, and  $\approx$ 1.51 V, respectively. The estimated open-circuit voltage for the five-subcell photovoltaic solar cell **700**  $(V_{oc}=V_{oc1}+V_{oc2}+V_{oc3}+V_{oc4}+V_{oc5})$  was  $\approx$ 5.39 V.

[0091] The calculated optimal first short-circuit photocurrent density ( $I_{sc1}$ ) for the first subcell 722, second short-circuit photocurrent density ( $I_{sc2}$ ) for the second subcell 724, third short-circuit photocurrent density ( $I_{sc3}$ ) for the third subcell 726, fourth short-circuit photocurrent density ( $I_{sc3}$ ) for the fourth subcell 728, and fifth short-circuit photocurrent density ( $I_{sc5}$ ) for the fifth subcell 730 are  $\approx$ 40 mA/cm²,  $\approx$ 27 mA/cm²,  $\approx$ 19 mA/cm²,  $\approx$ 15 mA/cm², and  $\approx$ 13 mA/cm², respectively. From these numerical calculations, the estimated series-matched current density ( $I_{sc}$ ) for the five-junction photovoltaic solar cell 700 was approximately 13 mA/cm²,

 $\mathbf{I}_{sc} = \mathbf{I}_{TJ1} = \mathbf{I}_{TJ2} = \mathbf{I}_{TJ3} = \mathbf{I}_{TJ3} = \mathbf{I}_{TJ4} = \mathbf{I}_{sc1} = \mathbf{I}_{sc2} = \mathbf{I}_{sc3} = \mathbf{I}_{sc4} = \mathbf{I}_{sc5} \text{ as discussed above}.$ 

[0092] The estimated ideal series-interconnected efficiency  $(\eta=\eta_1+\eta_2+\eta_3+\eta_4+\eta_5)$  for the five-subcell photovoltaic solar cell 700 was at least  $\approx$ 50% under 500 suns. As described above for other embodiments of the invention,  $(p^{-+})ZnTe/(n^{++})ZnTe$  tunnel junctions may be placed between the subcells to improve light conversion efficiency.

[0093] The first subcell 722, second subcell 724, third subcell 726, fourth subcell 728, and fifth subcell 730 of this homo-junction photovoltaic solar cell 700 can be replaced with hetero-junction subcells to further improve the performance by minimizing the absorption in the first emitter 703, second emitter 707, third emitter 711, fourth emitter 715, and fifth emitter 719 while maximizing the absorption in the first base 702 of first subcell 722, second base 706 of the second subcell 724, third base 710 of the third subcell 726, fourth base 714 of the fourth subcell 728, and fifth base 718 of the fifth subcell 730.

**[0094]** Moreover, the fifth (n+)Cd<sub>1-z</sub>Zn<sub>z</sub>Te emitter **719** of the fifth subcell **730** can be replaced with a higher energy gap alloys such as (n+)ZnTe emitter (E<sub>g4E</sub>=1.8 to 2.26 eV), (n+) CdS emitter (E<sub>g5E</sub>=2.46 eV), (n+)ZnSe emitter (E<sub>g5E</sub>=2.72 eV), (n+)MgTe emitter (E<sub>g5E</sub>=3.40 eV), (n+)ZnS emitter (E<sub>g5E</sub>=3.73 eV), (n+)CdZnTe emitter (E<sub>g5E</sub>=1.8 to 2.26 eV), (n+)CdMnTe emitter (E<sub>g5E</sub>=1.8 to 2.92 eV), or (n+)CdMgTe

emitter ( $E_{g5E}\approx1.8$  to 3.40 eV) to allow more incident light to reach the (p–)Cd<sub>1-z</sub>Zn<sub>z</sub>Te base **718** ( $E_{g5E}\approx2.00$  eV) in order to increase the photo-generation of electron-hole pairs and hence increase the photocurrent of the fifth subcell **730**.

**[0095]** Additionally, the fifth semiconductor base may be alloys of CdZnTe ( $E_{g5E}\approx1.8-2.26$  eV) or CdMgTe ( $E_{g5E}\approx1.8-3.2$  eV).

[0096] Numerical modeling was performed for a heterointerface three-junction photovoltaic solar cell having the following top-to-bottom composition: (n+)ZnO/(n+)ZnTe/(p-)Cd<sub>1-z</sub>Zn<sub>z</sub>Te/(p<sup>++</sup>)MgTe/(n+)ZnTe/(p-)Cd<sub>1-z</sub>n<sub>z</sub>Te/(p<sup>++</sup>)MgTe/(n+)MgTe/(n+)MgTe/(n+)ZnTe/(p-)Si. The calculated first open-circuit photovoltage ( $V_{oc1}$ ) for the first subcell 722, second open-circuit photovoltage ( $V_{oc2}$ ) for the second subcell 724, third open-circuit photovoltage ( $V_{oc2}$ ) for the second subcell 726, fourth open-circuit photovoltage ( $V_{oc3}$ ) for the third subcell 726, fourth open-circuit photovoltage ( $V_{oc4}$ ) for the fourth subcell 730 were  $\approx 0.50 \, \text{V}$ ,  $\approx 0.89 \, \text{V}$ ,  $\approx 1.11 \, \text{V}$ ,  $\approx 1.36 \, \text{V}$ , and  $\approx 1.51 \, \text{V}$ , respectively. The estimated open-circuit voltage ( $V_{oc} = V_{oc1} + V_{oc2} + V_{oc3} + V_{oc4} + V_{oc5}$ ) for the hetero-interface five-junction photovoltaic solar cell 700 was  $\approx 5.37 \, \text{V}$ .

[0097] The calculated optimal first short-circuit photocurrent density  $(I_{sc1})$  for the first subcell 722, second short-circuit photocurrent density  $(I_{sc2})$  for the second subcell 724, third short-circuit photocurrent density  $(I_{sc3})$  for the third subcell 726, fourth short-circuit photocurrent density  $(I_{sc4})$  for the fourth subcell 728, and fifth short-circuit photocurrent density  $(I_{sc5})$  for the fifth subcell 730 were  $\approx$ 40 mA/cm²,  $\approx$ 27 mA/cm²,  $\approx$ 19 mA/cm²,  $\approx$ 15 mA/cm², and  $\approx$ 13 mA/cm², respectively. In this case, the estimated series-matched short-circuit photocurrent density  $(I_{sc})$  for the five-junction photovoltaic solar cell 700 again was approximately 13 mA/cm², and  $I_{sc}=I_{TJ1}=I_{TJ2}=I_{TJ3}=I_{TJ4}=I_{sc1}=I_{sc2}=I_{sc3}=I_{sc4}=I_{sc5}$  as discussed above

[0098] The estimated ideal series-interconnected efficiency  $(\eta=\eta_1+\eta_2+\eta_3+\eta_4+\eta_5)$  for the hetero-interface five-subcell photovoltaic solar cell 700 again was at least ~55% under 500 suns. In this particular example,  $(p^{++})MgTe/(n^{++})MgTe$  tunnel junctions were placed between the subcells to improve the light conversion efficiency. The antireflection coating 720, which may comprise of more than one thin layer, can be made of materials with energy gaps that are greater than the energy gap of the emitter 719 of the fifth subcell 730 ( $E_{gARC} > E_{g5E}$ ). For instance, the antireflection coating can be made of an (n+)MgTe ( $E_{gARC} > 3.40$  eV) semiconductor thin layer.

[0099] FIG. 8 shows a five-subcell solar cell 800 which can have the following top-to-bottom composition: (n+)ZnO/  $_{y}Zn_{y}Te/(n+)Cd_{1-x}Zn_{x}Te/(p-)Cd_{1-x}Zn_{x}Te/(n+)CdTe/(p-)$ CdTe/(n+)Si/(p-)Si. Cell 800 does not have tunnel junctions between its subcells. In this example, the first subcell 814, which is made of a first, preferably Group IV material system, more preferably comprises a first (p-)Si base layer 802 and a first (n+)Si emitter layer 803 having a first base energy gap  $(E_{g1B}\approx 1.10 \text{ eV})$ , a first emitter energy gap  $(E_{g1E}\approx 1.10 \text{ eV})$ , and a first layer thickness (d<sub>1</sub>≈1.0 to 500 µm, preferably greater than or equal to 2 µm). The second subcell 815, which is disposed immediately adjacent to the first subcell 814 and is made of a second, preferably Group II-VI material system, comprises a second (p-)CdTe base layer 804 and a second (n+)CdTe emitter layer 805 having a second base energy gap  $(E_{g2B}\approx 1.51 \text{ eV})$ , second emitter energy gap  $(E_{g2E}\approx 1.51 \text{ eV})$ ,

and a second layer thickness ( $d_2\approx0.5$  to 15 µm, preferably 2-6 µm). The third subcell **816**, which is disposed immediately adjacent to the second subcell **815** and is made of a third, preferably Group II-VI material system, comprises a third (p-)Cd<sub>1-x</sub>Zn<sub>x</sub>Te base layer **806** and a third (n+)Cd<sub>1-x</sub>Zn<sub>x</sub>Te emitter layer **807** having a third base energy gap ( $E_{g3B}\approx1.71$  eV), a third emitter energy gap ( $E_{g3E}\approx1.71$  eV), and a third layer thickness ( $d_3\approx0.1$  to 10 µm, preferably 2 to 6 µm).

[0100] The fourth subcell 817, which is disposed immediately adjacent to the third subcell 816 and is made of a fourth, preferably II-VI material system, more preferably comprises a fourth  $(p-)Cd_{1-}$ , Zn, Te base layer 808 and a fourth  $(n+)Cd_{1-}$ yZn, Te emitter layer 809 having a fourth base energy gap  $(E_{g4B}\approx 1.91 \text{ eV})$ , a fourth base energy gap  $(E_{g4E}\approx 1.91 \text{ eV})$ , and a fourth layer thickness (d<sub>4</sub>≈0.1 to 10 µm, preferably 2 to 6 um). The fifth subcell **818**, which is disposed immediately adjacent to the fourth subcell 817 and is made of a fifth, preferably Group II-VI material system, more preferably comprises a fifth (p-)Cd<sub>1-z</sub>Zn<sub>z</sub>Te base layer 810 and a fifth (n+)Cd<sub>1-z</sub>Zn<sub>z</sub>Te emitter layer **811** having a fifth base energy gap ( $E_{e5B} \approx 2.00 \text{ eV}$ ), a fifth emitter energy gap ( $E_{e5E} \approx 2.00 \text{ eV}$ ) eV), and a fifth layer thickness (d<sub>4</sub>≈0.1 to 10 μm). The first subcell 814, second subcell 815, third subcell 816, fourth subcell 817, and fifth subcell 818 of the homo-junction photovoltaic solar cell 800 can be replaced with hetero-junction subcells as described above to further improve overall absorption of incident light.

[0101] In another variation of the fourth embodiment of the present invention, the (p-) and (n) semiconductor layers of cell 800 are reversed.

[0102] The invention discloses, for the first time, several monolithic multi-subcell photovoltaic solar cells having no Group III-V semiconductors and having ideal overall series efficiencies of at least 45% under concentrated sunlight of approximately 500 suns. These ideal energy conversion efficiencies have not been reported before for solar cells composed of any monatomic or compound semiconductor family or combination of such families or material systems (Groups IV, III-V, or II-VI).

[0103] In summary, several monolithic multi-junction or -subcell photovoltaic solar cells have been described which are fabricated of a combination of Group IV and Group II-VI materials, preferably on silicon substrates. Species, alloys, and thicknesses of successively grown layers can be selected to create solar cells having more than fifty percent ideal overall energy conversion efficiencies.

[0104] While particular preferred embodiments of the present invention have been presented in detail hereinabove for the purposes of description and illustration, it will be understood by those skilled in the art that all suitable modifications, alterations, substitutions, equivalent arrangements, and enhancements of the preferred embodiments may be made without departing from the spirit and broader scope of the invention. In particular, the Si substrate can be lifted off or thinned, an epitaxial Ge layer may be grown on the back of thinned Si for better absorption of infrared light before the epitaxial II-VI layers are grown on the opposite face of the Si, the Si substrate can be replaced by a Ge substrate or other substrate-related modifications to the preferred embodiments may be made.

We claim:

- 1. A monolithic photovoltaic solar cell with multiple subcells, comprising:
  - a first subcell including:
    - a first base formed of a semiconductor to be of a first conductivity type;
    - a first emitter formed to adjoin the first base and formed of a semiconductor having a second conductivity type opposite the first conductivity type;
  - a second subcell adjacent to the first subcell and including:
  - a second base formed of a semiconductor of the first conductivity type;
    - a second semiconductor emitter of the second conductivity type formed to adjoin the second base;
    - wherein at least one of the first and second bases and the first and second emitters is formed of a Group IV semiconductor material;
    - wherein at least one of the first and second bases and the first and second emitters is formed of a Group II-VI semiconductor material;
    - the second subcell generating a second short-circuit current density responsive to solar radiation of a predetermined intensity incident on a face of the second subcell opposed to the first subcell;
    - the first subcell generating a first short-circuit current density responsive to the solar radiation which has passed through the second subcell into the first subcell, the first short-circuit current density being substantially equal to said second short-circuit current density.
- 2. The solar cell of claim 1, wherein the Group IV semiconductor material is selected from the group consisting of silicon, germanium, and silicon-germanium.
- 3. The solar cell of claim 1, wherein the first conductivity type is n-type.
- **4**. The solar cell of claim **1**, wherein the first conductivity type is (p–)type.
- **5.** The solar cell of claim **1**, wherein the Group II-VI semiconductor material is selected from the group consisting of CdS, CdTe, CdSe, ZnTe, ZnSe, ZnS, MgTe, CdSeTe, CdZnTe, CdMnTe, CdMgTe, and CdHgTe.
- **6.** The solar cell of claim **1**, further comprising a first tunnel junction between said first and second subcells.
- 7. The solar cell of claim 6, wherein the first tunnel junction comprises at least one semiconductor layer selected from the group consisting of ZnTe, ZnS, MgTe, CdZnTe, and CdMgTe.
- 8. The solar cell of claim 1, wherein said second subcell has a lower face proximate to the first subcell and an upper face remote from the first subcell, the second subcell further comprising a semiconductive antireflection layer formed to adjoin the upper face and comprising at least one material selected from the group consisting of Cd<sub>2</sub>SnO<sub>4</sub>, SnO<sub>2</sub>, ZnSe, TiO<sub>2</sub>, MgTe, ZnO, ZnS, MgSe, ITO, MgS, MgO, SiO<sub>2</sub>, and MgF<sub>2</sub>.
- 9. The solar cell of claim 1, wherein the first subcell has an upper face proximate the second subcell and a lower face remote from the second subcell, the solar cell further comprising a conductive back contact, disposed adjacent to the lower face of the first subcell.
- 10. The solar cell of claim 1, the second subcell having a lower face proximate to the first subcell and an upper face remote from the first subcell and a conductive front contact formed adjacent to the upper face of the second subcell.

- 11. The solar cell of claim 1, wherein the first base is formed from a Group IV semiconductor selected from the group consisting of Si, Ge and Si—Ge.
  - 12. The solar cell of claim 1, further comprising:
  - a third subcell formed over the second subcell and formed to be opposed to the first subcell, the third subcell comprising:
    - a third base formed of a semiconductor material to be of the first conductivity type;
    - a third emitter formed of a semiconductor material to be of the second conductivity type and formed to adjoin the third base, at least one of the third base and third emitter being formed of a Group II-VI semiconductor material:
    - the third subcell generating a third open-circuit current density responsive to said solar radiation which matches substantially said first and second short-circuit current densities.
- 13. The solar cell of claim 12, wherein the Group II-VI semiconductor material forming at least one of the third base and third emitter is selected from the group consisting of CdS, CdTe, CdSe, ZnTe, ZnSe, ZnS, MgTe, CdSeTe, CdZnTe, CdMnTe, CdMgTe, and CdHgTe.
- 14. The solar cell of claim 12, further comprising a first tunnel junction between the first and second subcells and a second tunnel junction between the second and third subcells.
- 15. The solar cell of claim 14, wherein the second tunnel junction comprises at least one degeneratively alloyed semiconductor layer selected from the group consisting of ZnTe, ZnS, MgTe, CdZnTe, and CdMgTe.
- 16. The solar cell of claim 12, wherein said third subcell has a lower face proximate to the second subcell and an upper face remote from the second subcell, the cell further comprising a semiconductive antireflection layer formed over the third subcell upper face and comprising at least one material selected from the group consisting of Cd<sub>2</sub>SnO<sub>4</sub>, SnO<sub>2</sub>, ZnSe, TiO<sub>2</sub>, MgTe, ZnO, ZnS, MgSe, ITO, MgS, MgO, SiO<sub>2</sub>, and MgF<sub>2</sub>.
  - 17. The solar cell of claim 12, further comprising:
  - a fourth subcell formed over the third subcell and to be opposed to the first subcell, the fourth subcell comprising:
    - a fourth base formed of a semiconductor material to be of the first conductivity type;
    - a fourth emitter formed of a semiconductor material to be of the second conductivity type and formed to adjoin the fourth base, at least one of the fourth base and fourth emitter being formed of a Group II-VI semiconductor material;
    - the fourth subcell generating a fourth open-circuit current density responsive to said solar radiation which matches substantially said first, second, and third short-circuit current densities.
- **18**. The solar cell of claim **17**, wherein the Group II-VI semiconductor material forming at least one of the emitter and base of the fourth subcell is selected from the group consisting of CdS, CdTe, CdSe, ZnTe, ZnSe, ZnS, MgTe, CdSeTe, CdZnTe, CdMnTe, CdMgTe, and CdHgTe.
- 19. The solar cell of claim 17, further comprising a first tunnel junction between the first and second subcells, a second tunnel junction between the second and third subcells, and a third tunnel junction between the third and fourth subcells.

- **20**. The solar cell of claim **19**, wherein the third tunnel junction comprises at least one degeneratively alloyed Group II-VI semiconductor layer.
- 21. The solar cell of claim 17, wherein said fourth subcell further has a lower face proximate to the third subcell and an upper face remote from the third subcell, the fourth subcell further comprising a semiconductive antireflection layer formed to adjoin the fourth subcell upper face and comprising at least one material selected from the group consisting of Cd<sub>2</sub>SnO<sub>4</sub>, SnO<sub>2</sub>, ZnSe, TiO<sub>2</sub>, MgTe, ZnO, ZnS, MgSe, ITO, MgS, MgO, SiO<sub>2</sub>, and MgF<sub>2</sub>.
  - 22. The solar cell of claim 17 further comprising:
  - a fifth subcell formed over the fourth subcell and to be opposed to the first subcell, the fifth subcell comprising:
    - a fifth base formed of a semiconductor material to be of the first conductivity type;
    - a fifth emitter formed of a semiconductor material to be of the second conductivity type and formed to adjoin the fifth base, at least one of the fifth base and fifth emitter being formed of a Group II-VI semiconductor material:
    - the fifth subcell generating a fifth open-circuit current density responsive to said solar radiation which matches substantially said first, second, third, and fourth short-circuit current densities.
- 23. The solar cell of claim 22, wherein the Group II-VI semiconductor material forming at least one of the base and emitter of the fifth subcell is selected from the group consisting of CdS, CdTe, CdSe, ZnTe, ZnSe, ZnS, MgTe, CdSeTe, CdZnTe, CdMnTe, CdMgTe, and CdHgTe.
- 24. The solar cell of claim 23, further comprising a first tunnel junction between the first and second subcells, a second tunnel junction between the second and third subcells, a third tunnel junction between the third and fourth subcells, and a fourth tunnel junction between the fourth and fifth subcells.
- **25**. The solar cell of claim **24**, wherein the fourth tunnel junctions comprises at least one degeneratively alloyed Group II-VI layer selected from the group consisting of ZnTe, ZnS, MgTe, CdZnTe, and CdMgTe.
- 26. The solar cell of claim 22, wherein said fifth subcell has a lower face proximate to the fourth subcell and an upper face remote from the fourth subcell, the fifth subcell further comprising a semiconductive antireflection layer formed on the upper face and comprising at least one material selected from the group consisting of Cd<sub>2</sub>SnO<sub>4</sub>, SnO<sub>2</sub>, ZnSe, TiO<sub>2</sub>, MgTe, ZnO, ZnS, MgSe, ITO, MgS, MgO, SiO<sub>2</sub>, and MgF<sub>2</sub>.
- 27. A monolithic multijunction photovoltaic solar cell, comprising:
  - a first subcell including:
    - a first base formed of a semiconductor material to be of a first conductivity type and having a first base energy gap;
    - a first emitter formed of a semiconductor material to be of a second conductivity type opposite the first conductivity type, the first emitter formed to adjoin the first base and having a first emitter energy gap higher than the first base energy gap;
  - a second subcell formed over the first subcell and comprising:
    - a second base formed of a semiconductor material to be of the first conductivity type and to have a second base energy gap higher than the first base energy gap;

- a second emitter formed of a semiconductor material to be of the second conductivity type and formed to adjoin the second semiconductor base;
- wherein at least one of the first and second bases and the first and second emitters is formed of a Group IV semiconductor material;
- wherein at least one of the first and second bases and the first and second emitters is formed of a Group II-VI semiconductor material;
- wherein none of the emitters or bases are a Group III-V semiconductor material; and
- wherein an overall ideal series efficiency of the solar cell calculated under 500 suns incident solar radiation is at least approximately 40%.
- 28. The solar cell of claim 27, further comprising a first tunnel junction between the first and second subcells, at least one layer of the first tunnel junction having an energy gap greater than the energy gap of the first semiconductor base.
- **29**. The solar cell of claim **27**, wherein the first base is a substrate formed of a Group IV semiconductor material selected from the group consisting of Si, Ge and Si—Ge.
  - 30. The solar cell of claim 27, further comprising:
  - a third subcell formed over the second subcell comprising:
    - a third base formed of a semiconductor material to be of the first conductivity type and having a third base energy gap higher than the second base energy gap;
    - a third emitter formed of a semiconductor material to be of the second conductivity type and formed to adjoin the third base, the third emitter having a third emitter energy gap higher than the third base energy gap and the second emitter energy gap;
    - wherein at least one of the third base and third emitter is formed of a Group II-VI semiconductor material;
    - wherein neither the third base nor the third emitter is formed of a Group III-V semiconductor material; and
    - wherein an overall ideal series efficiency of the solar cell is at least approximately 40% under 500 suns illumination
- 31. The solar cell of claim 30, further comprising a first tunnel junction between the first and second subcells and a second tunnel junction between the second and third subcells, at least one layer of the second tunnel junction having an energy gap greater than the energy gap of the second semiconductor base.
  - 32. The solar cell of claim 30, further comprising:
  - a fourth subcell formed over the third subcell and comprising:
    - a fourth base formed of a semiconductor material of the first conductivity type and having a fourth base energy gap higher than the third base energy gap;
    - a fourth emitter formed of a semiconductor material of the second conductivity type and formed to adjoin the fourth base and having a fourth emitter energy gap higher than the fourth base energy gap and the third emitter energy gap;
    - wherein at least one of the fourth base and fourth emitter is formed of a Group II-VI semiconductor material;
    - wherein neither the fourth base nor the fourth emitter is formed of a Group III-V semiconductor material; and
    - wherein an overall ideal series efficiency of the solar cell is at least approximately 45% under 500 suns illumination.

- 33. The solar cell of claim 32, further comprising:
- a first tunnel junction between the first and second subcells, a second tunnel junction between the second and third subcells, and a third tunnel junction between the third and fourth subcells, at least one layer of the third tunnel junction having an energy band gap greater than the energy gap of the third semiconductor base.
- 34. The solar cell of claim 32, further comprising:
- a fifth subcell formed over the fourth subcell and comprising:
  - a fifth base formed of a semiconductor material to be of the first conductivity type and having a fifth base energy gap higher than the fourth base energy gap;
  - a fifth emitter formed of a semiconductor material to be of the second conductivity type formed to adjoin the fifth semiconductor base and having a fifth emitter energy gap higher than the fifth base energy gap and the fourth emitter energy gap;
  - wherein at least one of the fifth base or the fifth emitter is formed of a Group II-VI semiconductor material:
  - wherein neither the fifth base nor the fifth emitter is formed of a Group III-V semiconductor material; and
  - wherein an overall ideal series efficiency of the solar cell is at least approximately 50% under 500 suns illumination
- 35. The solar cell of claim 34, further comprising:
- a first tunnel junction between the first and second subcells, a second tunnel junction between the second and third subcells, a third tunnel junction between the third and fourth subcells, and a fourth tunnel junction between the fourth and fifth subcells, at least one layer of the fourth tunnel junction having an energy gap greater the energy gap of the fourth semiconductor base.
- **36**. A photovoltaic solar cell exhibiting an overall ideal series energy conversion efficiency of at least 45% under 500 suns illumination and containing no Group III-V semiconductors.
- 37. The solar cell of claim 36, wherein at least a portion of the solar cell comprises a Group II-VI semiconductor.
- **38**. The solar cell of claim **37**, wherein the cell includes a substrate formed of a Group IV semiconductor material selected from the group consisting of Si, Ge and mixtures thereof.
- 39. The solar cell of claim 36, where the solar cell comprises:
  - a first subcell comprising a first emitter and a first base;
  - a second subcell comprising a second emitter and a second base and formed over the first emitter;
  - a third subcell comprising a third emitter and third base and formed over the second emitter; and
  - a fourth subcell comprising a fourth emitter and fourth base and formed over the third emitter.
- **40**. The solar cell of claim **39**, further comprising a first tunnel junction between the first and second subcells, at least one layer of the first tunnel junction having a higher energy gap than the first base.
- **41**. The solar cell of claim **39**, further comprising a second tunnel junction between the second and third subcells, at least one of the second tunnel junction layers having a higher energy gap than the second base.
- **42**. The solar cell of claim **39**, further comprising a third tunnel junction between the third and fourth subcells, at least one of the third tunnel junction layers having a higher energy gap than the third base.

- **43**. The solar cell of claim **39**, wherein at least one of the first, second, third, and fourth semiconductor bases is a Group IV semiconductor.
- **44**. The solar cell of claim **43**, wherein at least one emitter or base is formed of a Group II-VI semiconductor material.
- 45. The solar cell of claim 39, wherein the solar cell further comprises:
- a fifth subcell comprising a fifth emitter and a fifth base and formed over the fourth emitter;
- wherein an overall ideal series efficiency of the solar cell is at least approximately 55% under 500 suns illumination.
- **46**. The solar cell of claim **45**, wherein at least one of the fifth emitter or fifth base is formed of a Group II-VI semiconductor material.
- **47**. The solar cell of claim **45**, wherein the solar cell further comprises a fourth tunnel junction between the fourth and fifth subcells.
- **48**. A monolithic multijunction photovoltaic solar cell, comprising:
  - a first subcell including:
    - a first base formed of a semiconductor material to be of a first conductivity type and having a first base energy gap;
    - a first emitter formed of a semiconductor material to be of a second conductivity type opposite the first conductivity type and to adjoin the first base, the first emitter having a first emitter energy gap higher than the first base energy gap;
  - a second subcell formed over the first subcell and comprising:
    - a second base formed of Group II-VI semiconductor material to be of the first conductivity type and having a second base energy gap higher than the first base energy gap; and
    - a second emitter formed of Group II-VI semiconductor material to be of the second conductivity type formed to adjoin the second base and having a second emitter energy gap higher than the second base energy gap.
- **49**. The solar cell of claim **48**, wherein first base is formed of Group IV semiconductor material.
- **50**. The solar cell of claim **48**, wherein the first semiconductor base is alloyed to provide a high conductivity.
- 51. The solar cell of claim 48, wherein the first conductivity type is (n) type.
- 52. The solar cell of claim 48, wherein the first conductivity type is (p) type.
- **53**. The solar cell of claim **48**, wherein the first emitter comprises a semiconductor layer selected from the group consisting of Si, Ge, CdTe, CdSe, ZnTe, CdSeTe, CdZnTe, CdMnTe, CdMgTe, and CdHgTe semiconductors.
- **54**. The solar cell of claim **53**, wherein the first semiconductor emitter is selected from the group consisting of CdSeTe alloyed to exhibit an energy gap of approximately 1.51 to 1.7 eV, CdZnTe alloyed to exhibit an energy gap of approximately 1.51 to 2.26 eV, CdMnTe alloyed to exhibit an energy gap of approximately 1.51 to 2.92 eV, CdMgTe alloyed to exhibit an energy gap of approximately 1.51 to 3.2 eV, and CdHgTe alloyed to exhibit an energy gap of approximately 1.3 to 1.6 eV.
- **55**. The solar cell of claim **48**, wherein the second base comprises a material selected from the group consisting of CdTe, CdSe, CdSeTe, CdZnTe, CdMgTe, and CdHgTe.
- **56.** The solar cell of claim **55**, wherein the second base is selected from the group consisting of CdSeTe alloyed to

- exhibit an energy gap of approximately 1.51 to 1.7 eV, CdZnTe alloyed to exhibit an energy gap of approximately 1.51 to 2.0 eV, CdMgTe alloyed to exhibit an energy gap of approximately 1.51 to 2.0 eV for semiconductors, and CdHgTe alloyed to exhibit an energy gap of approximately 1.3 to 1.6 eV.
- **57**. The solar cell of claim **48**, wherein the second emitter comprises a material selected from the group consisting of CdTe, CdS, CdSe, ZnTe, ZnSe, ZnS, MgTe, CdSeTe, CdZnTe, CdMnTe, and CdMgTe.
- **58**. The solar cell of claim **57**, wherein the second emitter is selected from the group consisting of CdSeTe alloyed to exhibit an energy gap of approximately 1.51 to 1.7 eV, CdZnTe alloyed to exhibit an energy gap of approximately 1.51 to 2.26 eV, CdMnTe alloyed to exhibit an energy gap of approximately 1.51 to 2.92 eV, and CdMgTe alloyed to exhibit an energy gap of approximately 1.51 to 3.2 eV.
- **59**. The solar cell of claim **48**, further comprising a first tunnel junction between said first and second subcells, at least one layer of the first tunnel junction having an energy gap higher than said first base.
- **60**. The solar cell of claim **59**, wherein the first tunnel junction comprises at least one material selected from the group consisting of ZnTe, ZnS, MgTe, CdZnTe, and CdMgTe.
- **61**. The solar cell of claim **60**, wherein the first tunnel junction is formed of a semiconductor material selected from the group consisting of CdZnTe alloyed to exhibit an energy gap of approximately 2.0 to 2.26 eV and CdMgTe alloyed to exhibit an energy gap of approximately 2.0 to 3.2 eV.
- **62**. The solar cell of claim **48**, wherein the cell further comprises an antireflection layer formed over the second emitter and comprising a material selected from the group consisting of Cd<sub>2</sub>SnO<sub>4</sub>, SnO<sub>2</sub>, ZnSe, TiO<sub>2</sub>, MgTe, ZnO, ZnS, MgSe, ITO, MgS, MgO, SiO<sub>2</sub>, and MgF<sub>2</sub>, the energy gap of the antireflection layer being higher than the energy gap of the second emitter and the energy gap of the second base.
  - 63. The solar cell of claim 48, further comprising:
  - a third subcell formed over the second subcell and comprising:
    - a third base formed of a Group II-VI semiconductor material to be of the first conductivity type and having a third base energy gap higher than the second base energy gap; and
    - a third emitter formed of a Group II-VI semiconductor material of the second conductivity type and formed to adjoin the third semiconductor base and having a third emitter energy gap higher than the third base energy gap.
- **64**. The solar cell of claim **63**, wherein the third emitter comprises a semiconductor layer selected from the group consisting of CdS, CdSe, ZnTe, ZnSe, ZnS, MgTe, CdSeTe, CdZnTe, CdMnTe, and CdMgTe.
- **65**. The solar cell of claim **64**, wherein third emitter is selected from the group consisting of CdSeTe alloyed to exhibit an energy gap of approximately 1.60 to 1.7 eV, CdZnTe alloyed to exhibit an energy gap of approximately 1.6 to 2.26 eV, CdMnTe alloyed to exhibit an energy gap of approximately 1.6 to 2.92 eV, and CdMgTe alloyed to exhibit an energy gap of approximately 1.6 to 3.2 eV.
- **66**. The solar cell of claim **63**, wherein the third base comprises a material selected from the group consisting of CdSeTe, CdZnTe, and CdMgTe.

- **67**. The solar cell of claim **66**, wherein the third base is selected from the group consisting of CdSeTe alloyed to exhibit an energy gap of approximately 1.6 to 1.7 eV, CdZnTe alloyed to exhibit an energy gap of approximately 1.6 to 2.0 eV, and CdMgTe alloyed to exhibit an energy gap of approximately 1.6 to 2.0 eV.
- **68**. The solar cell of claim **63**, further comprising a second tunnel junction between said second and third subcells, at least one layer of the second tunnel junction having an energy gap higher than the energy gap of the third base.
- **69**. The solar cell of claim **67**, wherein the tunnel junction comprises a material selected from the group consisting of ZnTe, ZnS, MgTe, ZnS, CdZnTe, and CdMgTe.
- **70**. The solar cell of claim **68**, wherein said at least one layer of the second tunnel junction is selected from the group consisting of CdZnTe alloyed to exhibit an energy gap of approximately 2.0 to 2.26 eV and CdMgTe alloyed to exhibit an energy gap of approximately 2.0 to 3.2 eV.
  - 71. The solar cell of claim 63, further comprising:
  - a fourth subcell formed over the third subcell and comprising:
    - a fourth base formed of a Group II-VI semiconductor material to be of the first conductivity type and having a fourth base energy gap higher than the third base energy gap; and
    - a fourth emitter formed of a Group II-VI semiconductor material to be of the second conductivity type, formed to adjoin the fourth semiconductor base and having a fourth emitter energy gap higher than the fourth base energy gap.
- **72**. The solar cell of claim **71**, wherein the fourth emitter comprises a material selected from the group consisting of CdS, ZnTe, ZnSe, ZnS, CdMnTe, CdZnTe, and CdMgTe.
- **73**. The solar cell of claim **72**, wherein the fourth emitter material is selected from the group consisting of CdZnTe alloyed to exhibit an energy gap of approximately 1.8 to 2.26 eV, CdMnTe alloyed to exhibit an energy gap of approximately 1.8 to 2.92 eV, and CdMgTe alloyed to exhibit an energy gap of approximately 1.8 to 3.2 eV.
- **74**. The solar cell of claim **71**, wherein the fourth base comprises a material selected from the group consisting of CdZnTe and CdMgTe.
- **75**. The solar cell of claim **74**, wherein the fourth base material is selected from CdZnTe alloyed to exhibit an energy gap approximately 1.7 to 2.0 eV and CdMgTe alloyed to exhibit an energy gap of approximately 1.7 to 2.0 eV.
- **76**. The solar cell of claim **71**, further comprising a third tunnel junction between the third and fourth subcells, at least one layer of the third tunnel junction having an energy gap greater than the third base energy gap.
- 77. The solar cell of claim 76, wherein said at least one layer of the third tunnel junction comprises at least one material selected from the group consisting of ZnTe, ZnS, MgTe, ZnO, CdZnTe, CdMnTe, and CdMgTe.
- **78**. The solar cell of claim **77**, wherein said at least one layer of the third tunnel junction is selected from the group of CdZnTe alloyed to exhibit an energy gap of approximately 2.0 to 2.26 eV, CdMnTe alloyed to exhibit an energy gap of approximately 2.0 to 2.92 eV, and CdMgTe alloyed to exhibit an energy gap of approximately 2.0 to 3.2 eV.

- **79**. The solar cell of claim **71**, further comprising: a fifth subcell formed over the fourth subcell and compris
  - ing:
  - a fifth base formed of a Group II-VI semiconductor material to be of the first conductivity type and having a fifth base energy gap higher than the fourth base energy gap; and
  - a fifth emitter formed of a Group II-VI semiconductor material to be of the second conductivity type and having a fifth emitter energy gap higher than the fifth base energy gap.
- **80**. The solar cell of claim **79**, wherein the fifth base comprises a semiconductor material selected from the group consisting of CdS, ZnTe, ZnSe, ZnS, CdZnTe, CdMnTe, and CdMgTe.
- **81**. The solar cell of claim **80**, wherein the fifth base comprises a semiconductor material selected from the group consisting of CdZnTe alloyed to exhibit an energy gap of approximately 1.8 to 2.26 eV, CdMnTe alloyed to exhibit an energy gap of approximately 1.8 to 2.92 eV, and CdMgTe alloyed to exhibit an energy gap of approximately 1.8 to 3.2 eV.
- **82**. The solar cell of claim **79**, wherein the fifth emitter comprises a material selected from the group consisting of CdZnTe and CdMgTe semiconductors.

- **83**. The solar cell of claim **82**, wherein the fifth emitter is formed from a semiconductor material selected from the group consisting of CdZnTe alloyed to exhibit an energy gap of approximately 1.8 to 2.0 eV and CdMgTe alloyed to exhibit an energy gap of approximately 1.8 to 2.0 eV.
- **84**. The solar cell of claim **79**, further comprising a fourth tunnel junction between the fourth and fifth subcells.
- **85**. The solar cell of claim **84**, wherein at least one layer of the fourth tunnel junction comprises at least one material selected from the group consisting of ZnTe, ZnS, MgTe, ZnO, CdZnTe, and CdMgTe, said at least one layer of the fourth tunnel junction having an energy gap higher than the fifth base energy gap.
- **86**. The solar cell of claim **85**, wherein said at least one layer of the fourth tunnel junction is selected from a group consisting of CdZnTe alloyed to exhibit an energy gap of approximately 2.0 to 2.26 eV, CdMnTe alloyed to exhibit an energy gap of approximately 2.0 to 2.92 eV, and CdMgTe alloyed to exhibit an energy gap of approximately 2.0 to 3.4 eV.

\* \* \* \* \*